FINAL REPORT

ENERGY CONSERVATION IN INVESTMENT CASTING USING CANADIAN INDUSTRIAL MINERALS (UP-D-260)

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Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources, Canada.

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SUMMARY

This report describes the work performed under a contract from CANMET, Dept. of Energy, Mines and Resources (DSS File No. 15SQ23440-3-9001). The overall management of the program was done by Designed Precision Casting Inc. The technical portion of the program was carried out mainly at ORF in close collaboration with Designed Precision Casting Inc.

In this program, a laboratory process for the manufacture of ceramic shell molds at low firing temperature (600^{o}C) has been developed. This comprises the development of four promising slurry compositions (Table 5, page A28), to produce ceramic shell molds with substantial increase in strength. The fired strength of these ceramic mold materials fired at 600^{o}C is about 1300 psi as compared to about 800 psi of the standard industrial shell molds normally fired at 1,000^{o}C. The key to the above development lies in the successful identification,development and use of phosphate binders.

This report describes the results of the study made during Phase I of the program.

Because of its potential for significant economic benefits, the company would like to develop the manufacturing technology for making ceramic molds using the compositions developed in this phase. Hence, the company requests approval of phase II of this program, the details of which have been submitted separately.

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1. INTRODUCTION

The overall manufacturing cost of investment casting is directly related to the quality and cost of producing ceramic molds in the casting process. One way of reducing the cost is energy saving through low-temperature firing of ceramic shell molds. To reduce the energy requirement, it is desirable to have the ceramic molds made up of materials which can be fired at low temperatures. The development of such materials would be especially attractive for the casting of low melting temperature aluminum and copper alloys. An additional benefit can also be obtained by utilizing Canadian raw material where feasible.

In April, 1983, a research program supported by Energy, Mines and Resources was initiated at Designed Precision Casting Inc. (DPC) in conjunction with the Ontario Research Foundation (ORF). This project was directed towards conducting research into the preparation of ceramic shell molds which can be fired at low temperatures (800°C maximum) by substituting Canadian raw materials into the mold formulation.

This report summarizes the achievements accomplished in the period April 1 to July 31, 1983. The details of the experimental results of this project are presented in the final ORF report (Appendix A).

2. OBJECTIVES

The objectives of this program were:

Phase I To conduct research into the preparation of shell molds which can be fired at low temperatures (800°C maximum) by substituting Canadian raw materials into the mold formulation wherever feasible.

Phase II To develop the technology required to implement the fabrication of the shell mold formulation identified in Phase I.

This report summarizes the achievements accomplished during Phase I of the program. The following were the major tasks accomplished in achieving the set objectives of Phase I.

1. Preparation of the slurry compositions using Canadian substitute raw materials.

2. Preparation of Test Specimens.

3. Determination of Properties of Test Specimens.

4. Analysis of the property test data.

5. Metal Pouring Trial.

3. ACCOMPLISHMENTS

Listed below is a list of accomplishments in this project:

- Four promising slurry compositions were identified for further optimization and industrial implementation. (See Table 5, page A28).
- Development of a new laboratory process by which ceramic shell mold materials can be produced with the following advantages:
  - Low firing temperatures: the firing temperature is reduced from 1000°C to a temperature range of about 600-800°C.
  - High fired strength: the fired strength of the ceramic shell mold material is considerably improved over the standard industrial samples.
- Unique discovery and use of phosphate binders which enabled us to achieve the successful slurry compositions.

- Pouring of molten metal into ceramic shell molds was successfully carried out.

4. PROGRAM PROGRESS

4.1 Preparation of Slurry Using Canadian Substitute Raw Materials

Canadian raw materials such as nephiline syenite, fly ash, Quebec silica fume were utilized in the preparation of slurries using phosphate binders. Other raw materials evaluated were zircon and fused silica refractory flours. All these raw materials except nephiline syenite were successfully used in the preparation of trial slurries. Nephiline syenite slurries were rejected as they gelled after two days of mixing. (See Appendix A for experimental results).

4.2 Preparation of Test Specimen

Test strips and ceramic patterns were fabricated from the slurries as described in section 4.1. Table 1 summarizes the results of the selected strips dewaxed at Ontario Research Foundation and Designed Precision Casting Inc. Samples dewaxed at DPC using the steam autoclave required a special drying condition of ammonia atmosphere. Ammonia gas set the phosphate binder (mono-aluminum phosphate) at room temperature and produced samples with high green strength.

TABLE 1

The Effect of Drying Atmosphere

SLURRY	DRYING CONDITION	DEWAXED AT ORF (OVEN 140°C)	DEWAXED AT DPC (steam autoclave)
DA 45 (zircon/fused silica/MAP)	Ammonia atmosphere	Good strips	Good strips
- " -	Normal atmosphere	Good strips	Weak and soft samples

Fumed silica cup patterns dewaxed at DPC using the steam autoclave are shown in Figure 1.

The details of the experimental results of this major task are presented in Appendix A.

FIGURE 1

Fumed Silica Patterns
Dewaxed at DPC.

4.3 Determination and Analysis of Test Data

Cold and hot Modulus of Rupture Tests were conducted to determine the strength of the prepared shell molds. Thermal expansion coefficients of these samples were also determined.

The property test data were compiled and analyzed. The experimental results indicated that high strength samples can be prepared at low firing temperature (600°C - 800°C, 1 hr). The fired shell strength of the samples prepared from the slurry of zircon/fused silica and MAP* binder is about 1,300 psi as compared to about 800 psi of standard DPC samples. (See Appendix A for experimental results).

* MAP = Mono-aluminum phosphate.

4.4 Metal Pouring Trial

Ceramic shell molds were prepared from the slurry of zircon/fused silica refractory flours and mono-aluminum phosphate binder (DA45) for metal pouring trials. These ceramic molds were dried in a controlled atmosphere of ammonia and were dewaxed at DPC using the steam autoclave.

Molten aluminum was poured into these hollow ceramic shell molds which were broken away after the solidification of the aluminum (Figure 2). The preliminary results of the metal pouring trial were encouraging (Figure 3 and 4).

FIGURE 2

Ceramic Molds for Metal Pouring Trial

FIGURE 3: ALUMINUM CASTINGS

FIGURE 4: ALUMINUM CASTINGS

APPENDIX A

Ontario Research Foundation Report

Report No. 67064-82-4

DPC Low Firing

For

DESIGNED PRECISION CASTING INC.
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Attention: Mr. W.H. Breckenridge

FINAL REPORT

Date Issued: August 24, 1983

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1. INTRODUCTION

The process of investment casting is used in the manufacture of castings with very close tolerance limits. These castings may or may not need any further machining. The products made by investment casting are meant for a variety of uses, including those in defence, aircraft industry, nuclear reactors, chemical industry, etc..

Investment casting is highly energy intensive, since the ceramic molds are normally fired at 1,000°C. In order to reduce the energy requirement in the investment casting, it is desirable to have the ceramic molds made up of materials which can be fired at low temperatures. The development of such materials would be especially attractive for the casting of aluminum and low melting temperature copper alloy. The use of Canadian raw materials to replace the high cost of imported ones, was also of interest.

A program was initiated in April 1983, along with Design Precision Castings under the sponsorship of the Department of Energy, Mines and Resources. The objective of this program was to conduct research into preparation of shell molds which can be fired at low temperature (700°C max.) by substituting Canadian raw materials into the mold formulation.

This report describes the work carried out by the Ontario Research Foundation (ORF).

The experimental results in the first phase of the program showed that low firing (600°C) ceramic shell molds with high fired strength can be produced. By substituting phosphate binder, four promising slurry compositions were formulated. A new laboratory process was developed to produce ceramic shell mold materials.

2. PROGRAM PROGRESS

2.1 Preparation of Slurry Compositions Using Canadian Substitute Raw Material

Standard DPC refractory flours (zircon/fused silica) as well as Canadian raw materials such as nephiline syenite, fly ash, silica fume were used as raw materials in the preparation of trial slurries.

Nephiline Syenite is a granular igneous rock chiefly made up of nephiline (K_2O $3Na_2O$ $4Al_2O_3$ $6SiO_2$) and potash and soda feldspar. This material is readily available in the Peterborough region in Ontario. Silica fume and fly ash are waste materials from the manufacture of ferrosilicon and coal-fired electric powered stations, respectively.

The binders tested were phosphoric acid, magnesium phosphate (MGP) and mono-aluminum phosphate (MAP). These binders were selected because of their low-temperature bonding property (see Appendix A1) as well as their availability and low cost.

Gel tests were conducted to determine the gel characteristics of standard DPC flours and of Canadian raw materials with different binders.

The results presented in Table 1 indicate that mono-aluminum phosphate (MAP) is compatible as a binding agent for fly ash, silica fume, nephiline syenite as well as zircon/fused silica refractories. Phosphoric acid and MGP showed similar results.

2.1.1 Evaluation of Standard DPC Slurry Compositions Using Phosphate Binder

The compositions of testing slurries are presented in Table 2 and 3. Chemical additives such as wetting agent (ultrawet 60L, Alchem) and antifoaming agent (antifoam B, Emulsion Dow-Corning) were used to enhance the wetting properties and to reduce the foaming characteristics of the slurries respectively.

TABLE 1

Gel Test Results

Binder Binder Vol. (mL)	Refractory Flour (g)	Observation
MAP (50 mL)	Fumed silica (25 g)	26 days without gel
MAP (50 mL)	Nephiline Syenite (25 g)	26 days, solution is viscous
MAP (50 mL)	Flyash (25 g)	26 days without gel
MAP (50 mL)	MgO (25 g)	gelled with MgO after 1 day, suspended in lumps
Colloidal silica (50 mL) (Remasol SP 30)	Flyash (25 g)	gelled as mixed
Colloidal silica (50 mL)	Fumed silica (25 g)	gelled after the first day
Colloidal silica (50 mL)	Nephiline syenite (25 g)	several days without gel

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TABLE 2 - PRELIMINARY TRIAL SLURRIES

Date	Slurry No.	Refractory 1 (g)	Refractory 2 (g)	Binder 1 (ml)	Binder 2 (ml)	Chemical Additives (ml)	RW	Day 1 Viscosity Zahn cup #5 (sec)	Viscosity Zahn cup #5 (sec)	Day 2 Water/ chemical addition (ml)	New Viscosity Zahn cup #5 (sec)
April 14/83	P1	Zircon (1260)	Fused silica (840)	MAP	-	5 ml anti-foam		14	-	-	-
April 14/83	P2	Zircon (1520)	Fused silica (1080)	$HPO_3 \cdot 3H_2O$	Water (500)	-		12	7	Zircon 120 Fused Silica 80	13
April 22/83	P3	Quebec fumed silica (700)	-	MAP (1000)	-	-		12	13.5	-	-
April 22/83	P4	Flyash (900)	-	MAP (1000)	-	-		15	24	170 ml MAP	14
April 22/83	P5	Nepheline Syenite (~600)	-	MAP (1000)	-	-		Very viscous	Viscous	Day 4 MAP (350 ml)	15

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TABLE 3: Trial Slurries

Date	Slurry No.	Refractory 1 (g)	Refractory 2 (g)	Binder 1 (ml)	Binder 2 (ml)	Chemical Additives (ml)	RW	Day 1 Viscosity Zahn Cup #5 (sec)	Viscosity Zahn Cup #5 (sec)	Day 2 Water/ Chemical Addition (ml)	New Viscosity Zahn Cup #5 (sec)
Apr. 26/83	BEA1	Zircon Flour (2160)	Fused Silica (1440)	MAP (530)	Water (520)	Ultrawet 5 ml + H_2O 5ml		16	-	25 ml H_2O	16
May 4/83	BEA2	Zircon Flour (1845)	Fused Silica (1230)	MAP (710)	Water (310)	Ultrawet 2.5 ml + 2.5 ml H_2O		15.5	-	15 ml H_2O	16
May 4/83	BEA3	Zircon Flour (2220)	Fused Silica (1480)	MAP (310)	Water (700)	"		16		5 ml H_2O	16
May 4/83	BEA4	Zircon Flour (1320)	Fused Silica (880)	MAP (1010)	-	"		15.5	-	-	-
May 6/83	SS1	Zircon Flour (3750)	Fused Silica (2500)	SP30 Colloidal Silica 2150	-	-	0.125	11.5	-	-	-
May 10/83	BEM1	Zircon Flour (1530g)	Fused Silica (1020)	Magnesium Phosphate (1000)	-	10 ml anti-foam B + 40 ml H_2O & 5 ml ultra-wet 60L + 20 ml water		15	-	40 ml Mg Phosphate	16
May 10/83	BEM2	Zircon Flour (1780)	Fused Silica (1167)	Mg Phos-phate (700)	Water (300)	"		16	-	70 ml H_2O	16
May 10/83	BEM3	Zircon Flour (1930)	Fused Silica (1287)	Mg Phos-phate (500)	Water (500)	"		15	-	40 ml H_2O	15.5
May 10/83	BEM4	Zircon Flour (2080)	Fused Silica (1367)	Mg Phos-phate (300)	H_2O (700)	"		16	-	5 ml H_2O	16

Con't...

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TABLE 3: Trial Slurries Con't

Date	Slurry No.	Refractory 1 (g)	Refractory 2 (g)	Binder 1 (ml)	Binder 2 (ml)	Chemical Additives (ml) RW	Day 1 Viscosity Zahn Cup #5 (sec)	Viscosity Zahn Cup #5 (sec)	Day 2 Water/ Chemical Addition (ml)	New Viscosity Zahn Cup #5 (sec)
June 14/83	DA65	Zircon (2580)	Fused Silica (1,720)	MAP (975)	H_2O (555)	5 ml ultrawet + 7 ml H_2O	11	–	–	–
June 14/83	DA45	Zircon (2820)	Fused Silica (1880)	MAP (675)	H_2O (855)	–//–	11	–	–	–
June 14/83	DA25	Zircon (3120)	Fused Silica (2080)	MAP (375)	H_2O (1530)	–//–	11	–	–	–
June 14/83	DA15	Zircon (2760)	Fused Silica (1880)	MAP (225)	H_2O (1305)	–//–	10	–	–	–

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The standard DPC refractory flours (zircon/fused silica) were added to the solution until a viscosity in the range of 14 sec. (Zahr cup #5) were obtained. About two to three days of mixing were required to stabilize the viscosity and to remove all the air bubbles trapped in the slurries.

2.1.2 Preparation of Slurry Using Canadian Raw Materials

Trial slurries using Canadian raw materials were prepared and evaluated (Table 4). The refractories used were nephiline syenite, silica fume, and fly ash. These materials were added to monoaluminum phosphate (MAP) solution until a viscosity in the range of 10-14 sec (Zahn cup #5) was obtained. Antifoaming agent (Antifoam B, Emulsion, Dow-Corning) was added to silica fume slurries to reduce the foaming characteristics of these slurries.

Nephiline syenite slurries were rejected as they gelled after two days of mixing.

2.2 Preparation of Test Specimens

Test specimens were prepared from the slurries in Table 1, 2, 3 and 4. Facecoats of all samples were prepared from a standard DPC slurry (colloidal silica Remasol SP30 with zircon and fused silica flours) and stuccoed with zircon sand. The remaining coats of the test strips were prepared from the trial slurries and stuccoed with Molochite 30-80 (2 coats) and Molochite 16-30 (2 coats). Approximately two hours drying period was allowed between each coat.

All samples were fired at 600^{o}C for 1 hour. Green samples were dewaxed at 140^{o}C and 300^{o}C using the electric oven available at ORF. Samples with facecoats prepared from trial phosphate slurries were rejected because of the formation of a rough and porous inner surface.

TABLE 4

Trial Slurries Using Canadian Raw Materials

SLURRY NAME	REFRACTORY FLOURS	g	PHOSPHATE BINDER	ml	WATER (ml)	CHEMICAL ADDITIVE	VISCOSITY Zahn Cup #5 (Sec)
AFSA	Quebec Silica fume	1201	MAP	1330 (66%)	670	5 ml anti-foam 3+20 ml water	12
AFSB	Quebec Silica fume	1073	MAP	600 (46%)	700	"	15
AFSC	Quebec Silica fume	1625	MAP	420 (28%)	1080	"	13
AFSD	Quebec Silica fume	1620	MAP	130 (10%)	1170	"	15
AFAA	Fly Ash	1720	MAP	380 (21%)	1420	-	7.5
AFAB	Fly Ash	1600	MAP	620 (40%)	930	-	6.5
ANSA	Nephiline Syenite A270	1350	MAP	340 (7%)	1485	-	5.5
ANSB	Nephiline Syenite	1100	MAP	800 (40%)	1200	-	Slurry gelled
AFAC	Fly Ash	1070	MAP	1420 (90%)	160	-	13
AFAD	Fly Ash	1600	MAP	1015 (70%)	435	-	12
AFAE	Fly Ash	1980	MAP	600 (50%)	600	-	10
AFAF	Fly Ash	1550	MAP	405 (29%)	995	-	8

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2.2.1 Preparation of Test Specimens from Canadian Raw Material Slurries

Canadian raw materials such as fly ash and Quebec silica fume were successfully used to produce ceramic shell strips and ceramic shell molds.

Fumed silica strips had excellent dimensional stability (Fig. 5) but most of the ceramic shell molds cracked during the dewaxing process at 140°C.

Fly ash slurries of less than 50% vol. MAP did not produce any acceptable samples. All of the specimens prepared from these slurries dried very quickly before stuccoing. Ceramic shell molds with high strength and stable configuration (Fig. 6) were produced from fly ash slurries with high MAP concentration (~70% vol. MAP). Fly ash strips prepared from these high MAP slurries, however, warped upon firing (Fig. 7).

2.2.2 Preparation of Test Specimens Using Standard DPC Flours

Samples were fabricated from the slurries of zircon/fused silica refractories and phosphate binders (MAP and MGP). The two stuccoing materials successfully applied were Molochite and MgO (Figs. 8, 9 and 10). The experimental data are presented in Appendix A2.

Test strips with high phosphate binder content (>70% vol) warped during firing while samples with low phosphate binder concentration (<30% vol) dried very quickly before stuccoing and were thick. The optimum range of binder concentration was about 45-70% vol.

Specimens prepared from phosphoric acid slurry were very soft and sticky. These strips did not have any acceptable green strength and were rejected.

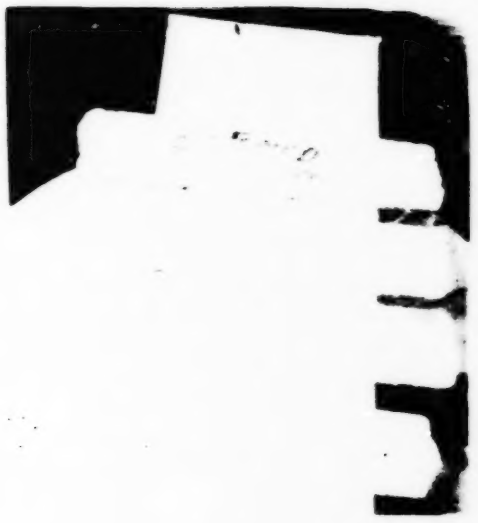


FIG. 5: Fumed Silica Samples

FIG. 6: Fly Ash/MAP/Molochite Patterns

FIG 7: Fly Ash Samples

FIG 8: Zircon/Fused Silica/MAP/MgO Patterns

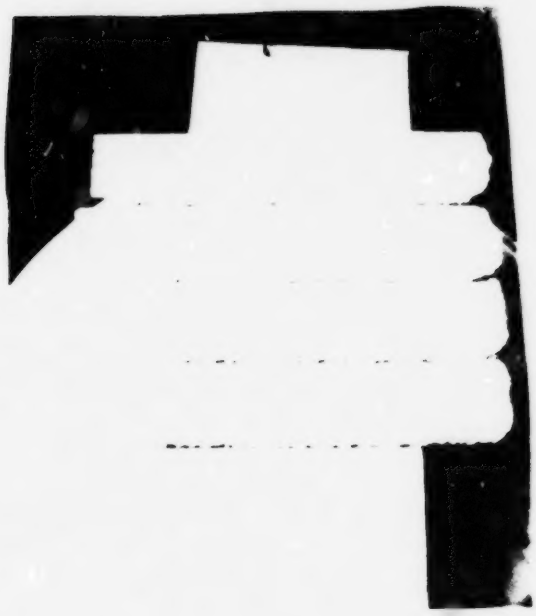


FIG. 9: Zircon/Fused Silica/MAP/Molochite Samples

FIG. 10: Zircon/Fused Silica/MAP/Molochite Patterns

Test strips prepared from phosphate binder slurry required long drying periods during the coating process (~2-4 hrs). It also needed about three to four days of drying in air before the dewaxing step. This is mainly because of the bonding characteristics of refractories and phosphate ion. The bonding reactions are believed to be similar to the reactions between alumina and phosphoric acid as follows:

$$Al_2O_3 + 6H_2PO_4 \longrightarrow 2Al(H_2PO_4)_3 + 6H_2O \quad (1)$$

$$Al(H_2PO_4)_3 \rightleftharpoons AlPO_4 \cdot xH_2O + 2H_3PO_4 \quad (2)$$

$$2Al(H_2PO_4)_3 \xrightarrow{257^oC} Al_2(H_2P_2O_7)_3 + 3H_2O \quad (3)$$

$$x Al_2(H_2P_2O_7)_3 \xrightarrow{500^oC} [Al(PO_3)_3]_x + 3/2\ xH_2O \quad (4)$$

The $Al(H_2PO_4)_3$ is water soluble and is very soft. The formation of $AlPO_4 \cdot xH_2O$ as in equation (2) will result in the hardening of the strips at the green stage. Therefore in order to provide acceptable green strength reaction (2) must be accelerated while its reverse reaction must be stopped or retarded to maintain $AlPO_4 \cdot xH_2O$. This can be accomplished by lowering phosphate concentration and by using chemical additives.

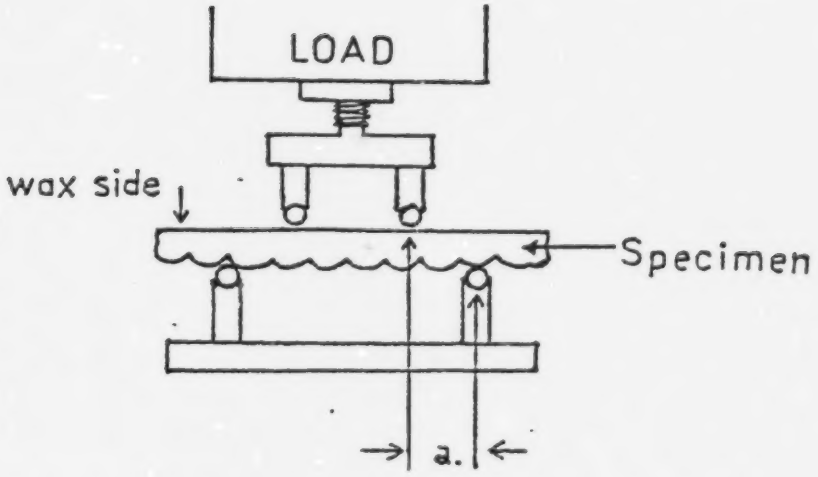
The chemical agents used were MgO as stuccoing macerials and ammonia gas during the drying process. Both MgO and ammonia gas significantly improved the green strength of the test strips.

2.3 Determination of Test Property

2.3.1 Cold MOR Test

The strengths of the test strips fabricated in Major Task 2.2 were evaluated at room temperature using an Instron Compressive strength unit equiped with a 4-point bending rig as outlined in Fig. 11. Figs. 12 to 14 present the cold modulus of rupture results of all the test strips prepared from the slurry of zircon/fused silica and phosphate binder. The cold strength of fly ash and silica fume samples are presented in Figs. 15 and

FIG. 11



$$\text{MOR (psi)} = \frac{3La}{bd^2}$$

where
- L = breaking load (pounds)
- a = distance between adjacent support and loading edges (inches)
- b = width of specimen (inches)
- d = thickness of specimen (inches)

Fig. 12 Mg Phosphate Binder
Stuccoing Material : MgO ——
Molochite —·—·—

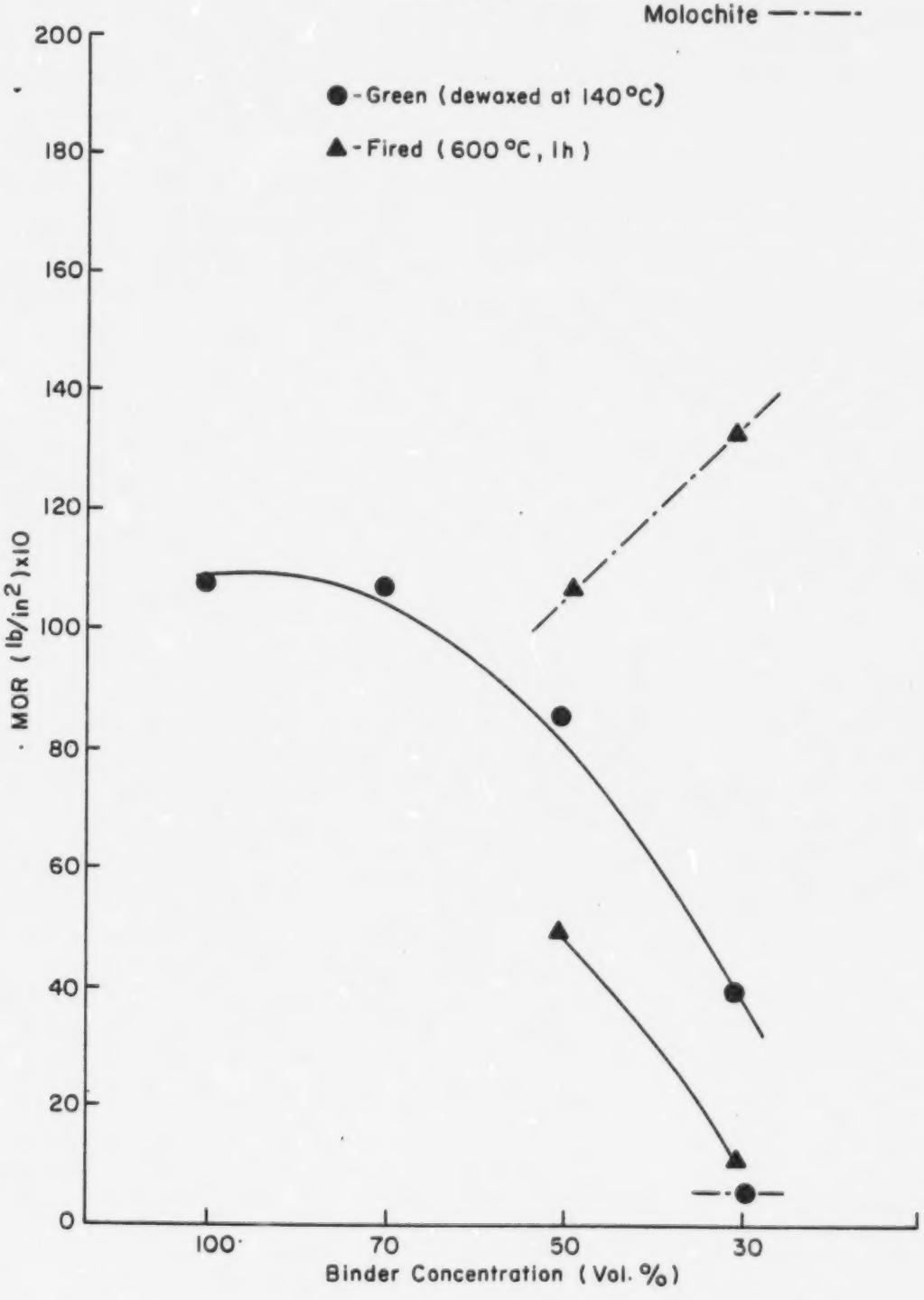


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Fig. 13 MAP Binder
Stuccoing Material: MgO

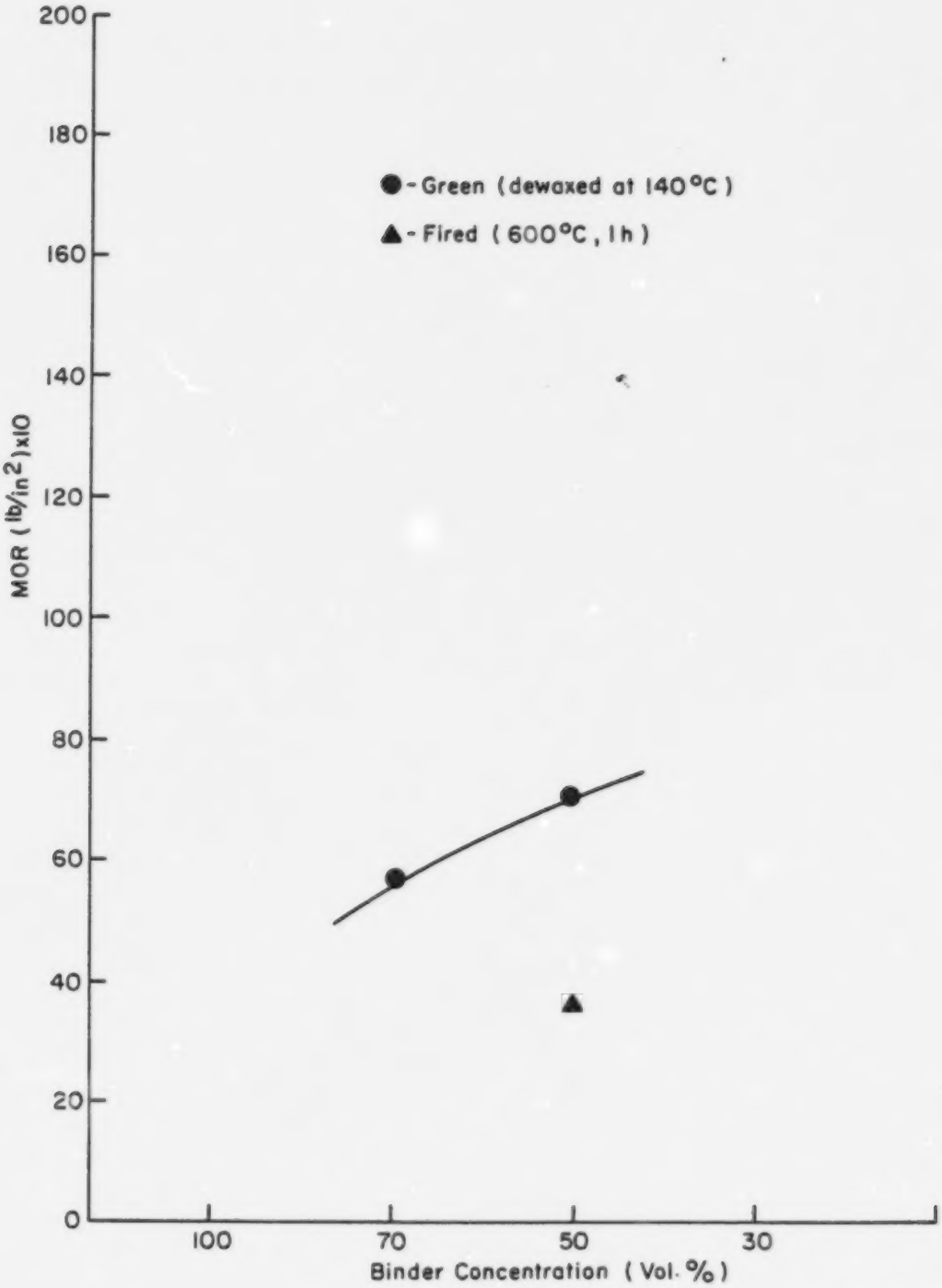

Fig. 14 MAP Binder
Stuccoing Material : Molochite

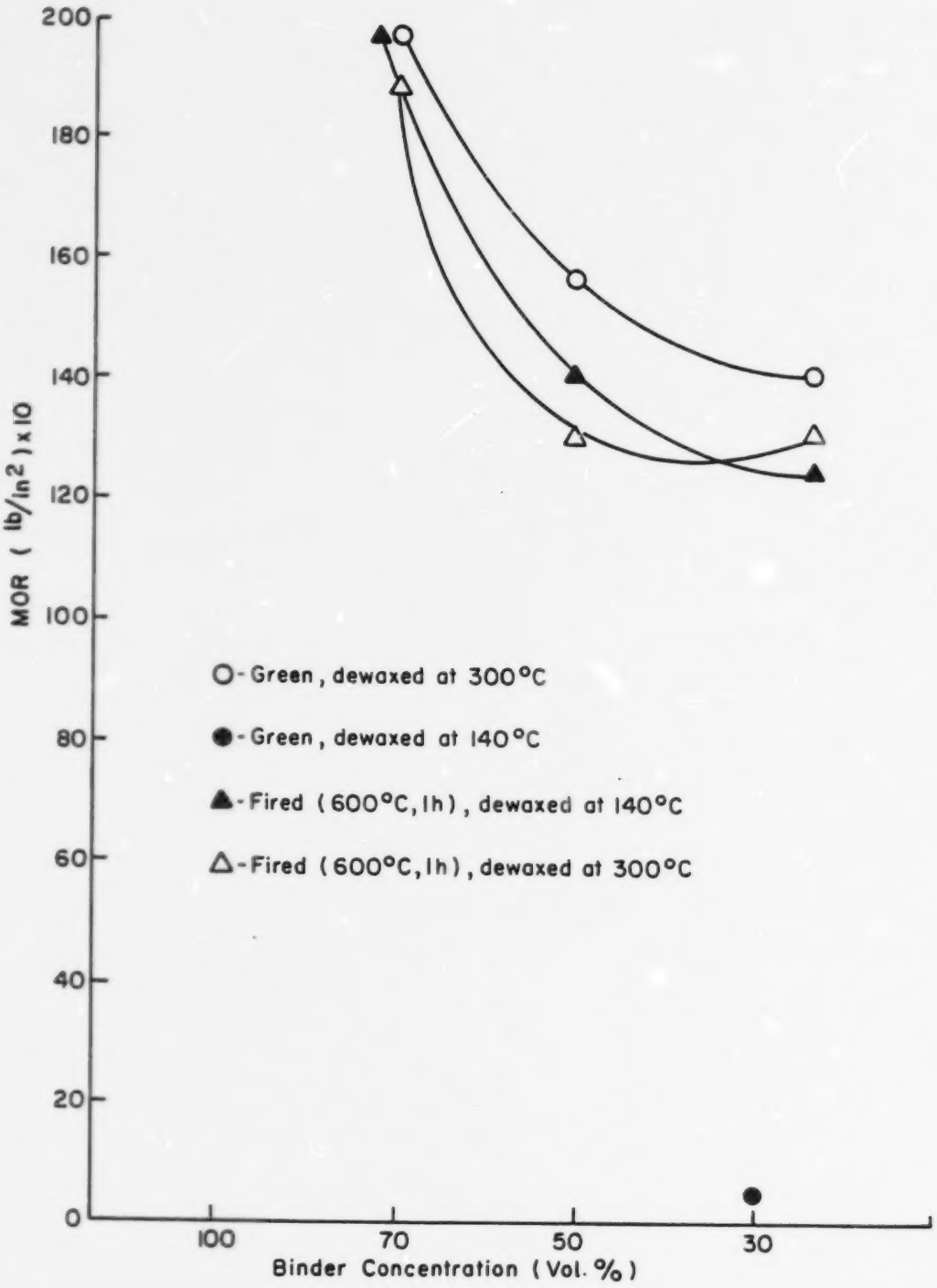

Fig. 15 MOR of Fly Ash Samples (Fired at 600°C, 1h)

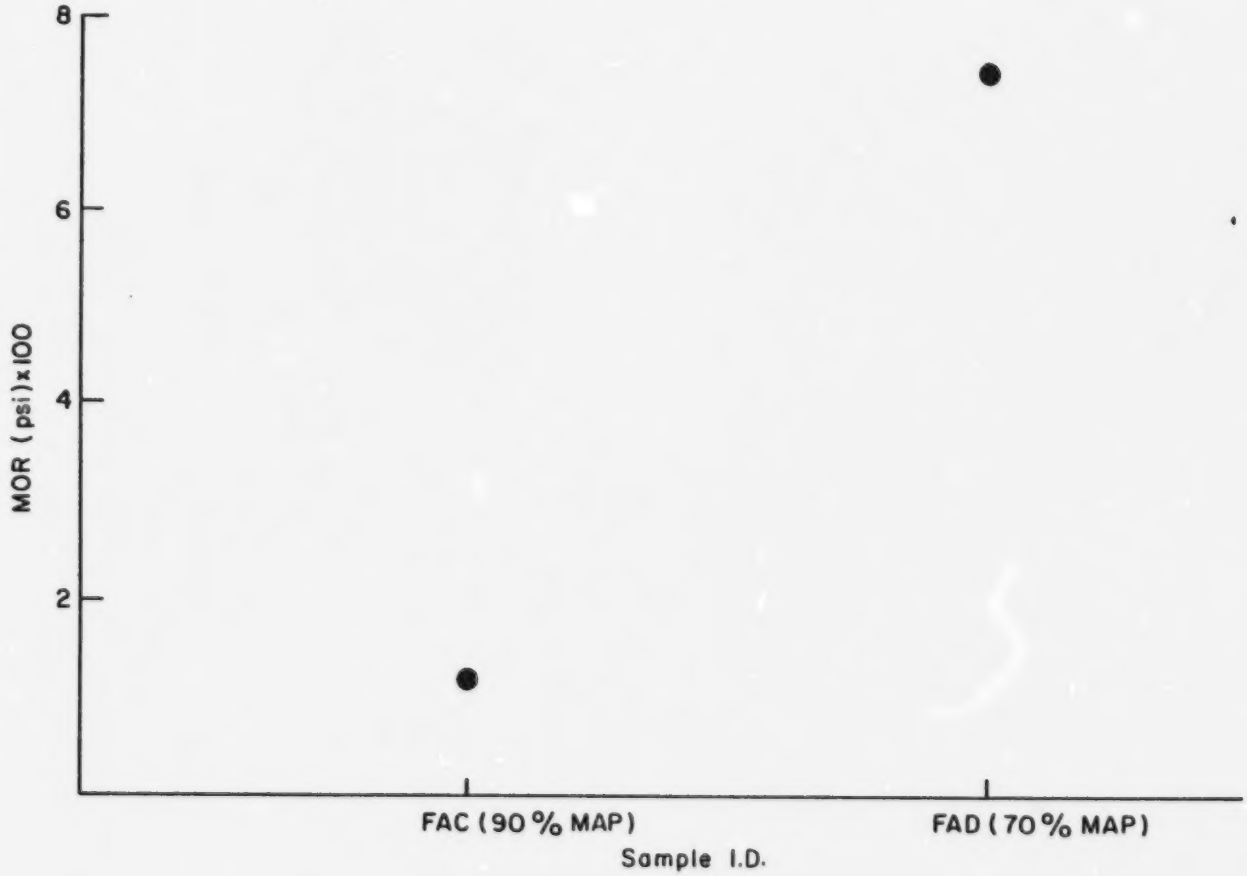

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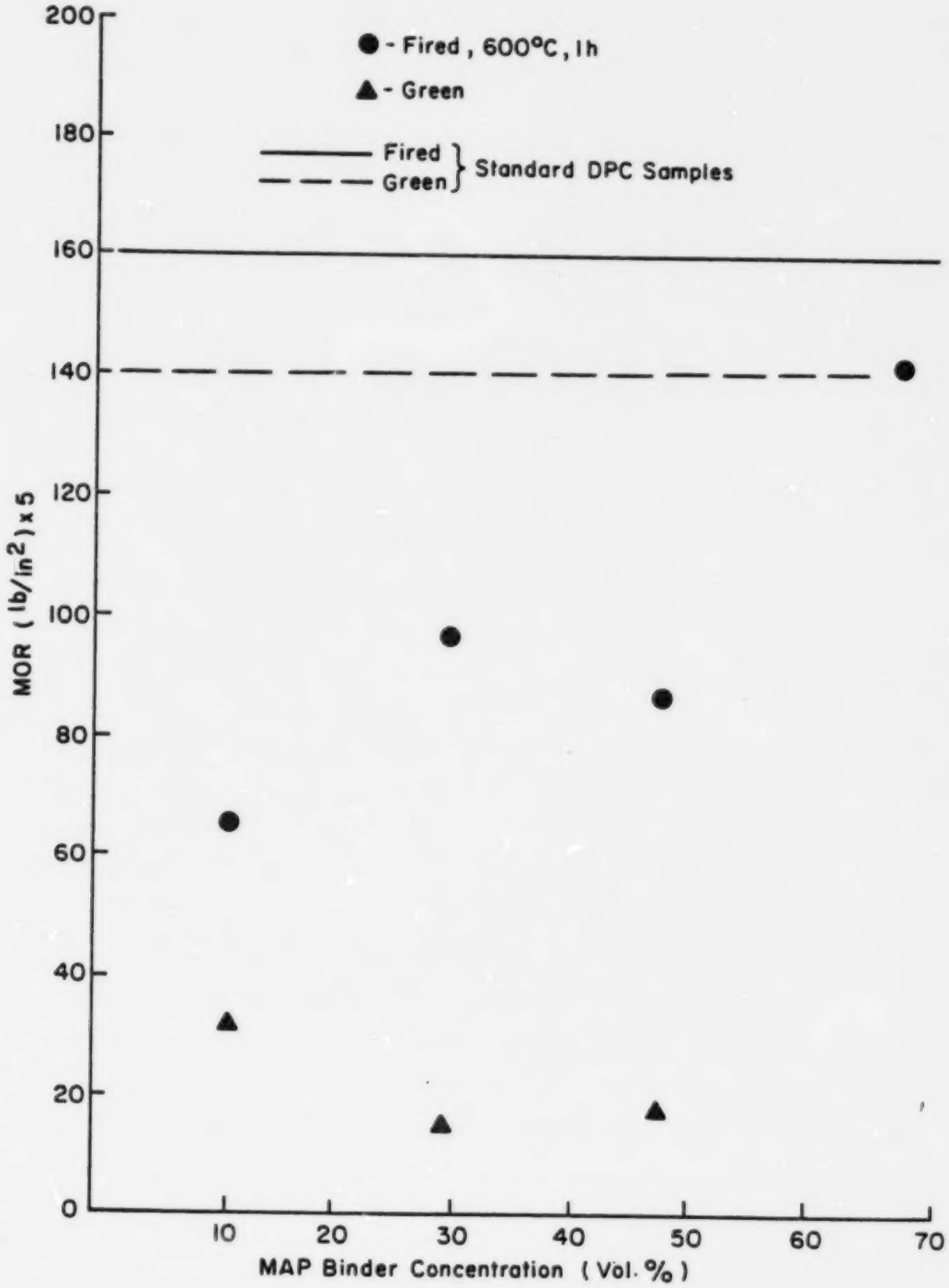
Fig. 16 Quebec Fumed Silica Samples
Stuccoing Material : Molochite



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16 respectively. The experimental data of the MOR tests are given in Appendix A2.

As can be observed in Figs. 12 and 13, samples stuccoed with MgO had acceptable green strength. MgO reacted with the phosphate binder at room temperature to form a strong bond at the green stage. The fired strengths of the strips stuccoed with MgO, however, were relatively weak.

Figure 14 summarizes the results of MAP binder and Molochite. Green strength (dewaxed at 140°C) is weak and fragile. Improvement of green strength is required for better handling at the green stage. Fired strength of these samples was exceptionally high - as high as 2,000 psi with 100% MAP concentration. However, at high MAP content, samples warped during the firing schedule.

Samples dewaxed at 300°C had high green strength (Fig. 14). This indicated that a bonding reaction occured at about 300°C or lower and higher firing temperature may not be necessary.

Fly ash and fumed silica specimens had low fired strength as compared to DPC standard samples. Both slurries performed best at low phosphate concentrations. Samples with high MAP content did not dry properly and had very low green strength. MOR data of fly ash and fumed silica samples are presented in Appendix A2.

2.3.2 Thermal Expansion

Thermal expansions of the test specimens were determined after the regular schedule of firing. The thermal expansion was measured using the apparatus available at ORF.

Rectangular samples of about 1"x¼"x¼" were prepared and the thermal expansion property was measured from 0 - 900°C.

The thermal expansion results of samples DA45 (zircon/fused silica/MAP/Molochite) and fly ash (fly ash/MAP/Molochite) are presented in Figs. 17 and 18 respectively. The thermal expansion coefficient of sample DA45 is about 3.207×10^{-6} cm/cm/K

2.3 Hot Strength

The hot MOR of the fired strips were measured at two different temperatures: 600°C and 800°C. These tests were performed using a hot modulus of rupture apparatus developed at ORF. The hot MOR results of DA compositions and fumed silica samples are plotted in Figs. 19 and 20. Data of these samples are presented in Appendix A2.

Fumed silica samples had similar hot strengths at both temperatures. This showed that higher firing temperature is not required for aluminum casting. In the case of DA specimens, the hot MOR at 800°C dropped significantly which indicated that higher firing temperature may be necessary for aluminum pouring trials.

2.4 Analysis of Property Test Data

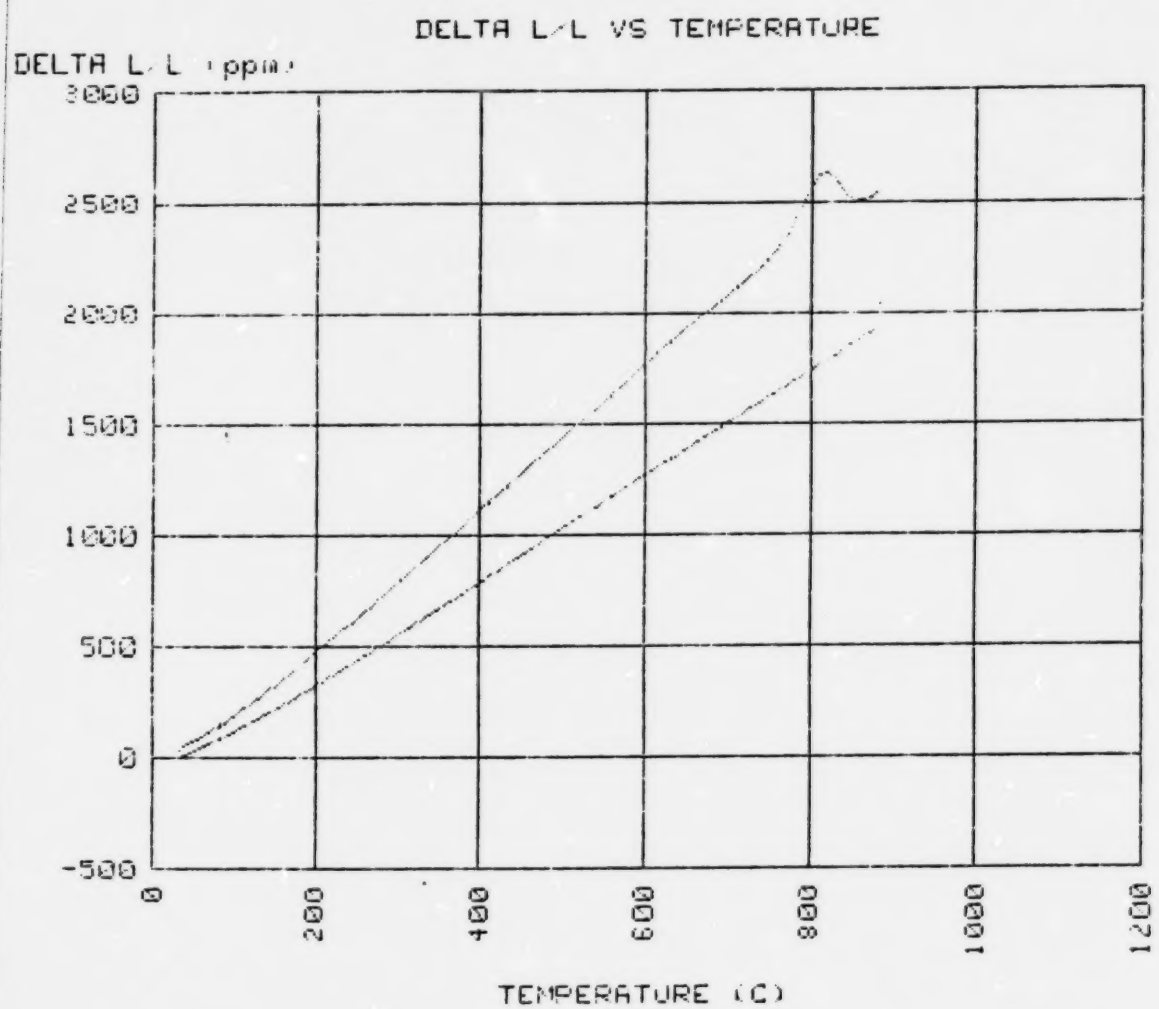
2.4.1 Analysis of Results

The experimental data were compiled and analyzed. The results can be summarized as follows:

1. MAP and MGP are comparable binding agents for zircon/fused silica refractories. For both binders, good ceramic specimens were obtained at binder concentrations of about 40-70% in volume (Figs. 12 and 14). Higher content of binders would leave them in excess with respect to the refractory which consequently softened the specimens.

FIG. 17: DA45 - Thermal Expansion

Date: 26:07:09:06:59 Sample: A22 DA-45



Softening Point: 813°C

Thermal Expansion Coefficient: 3.2070×10^{-6} cm/cm/K

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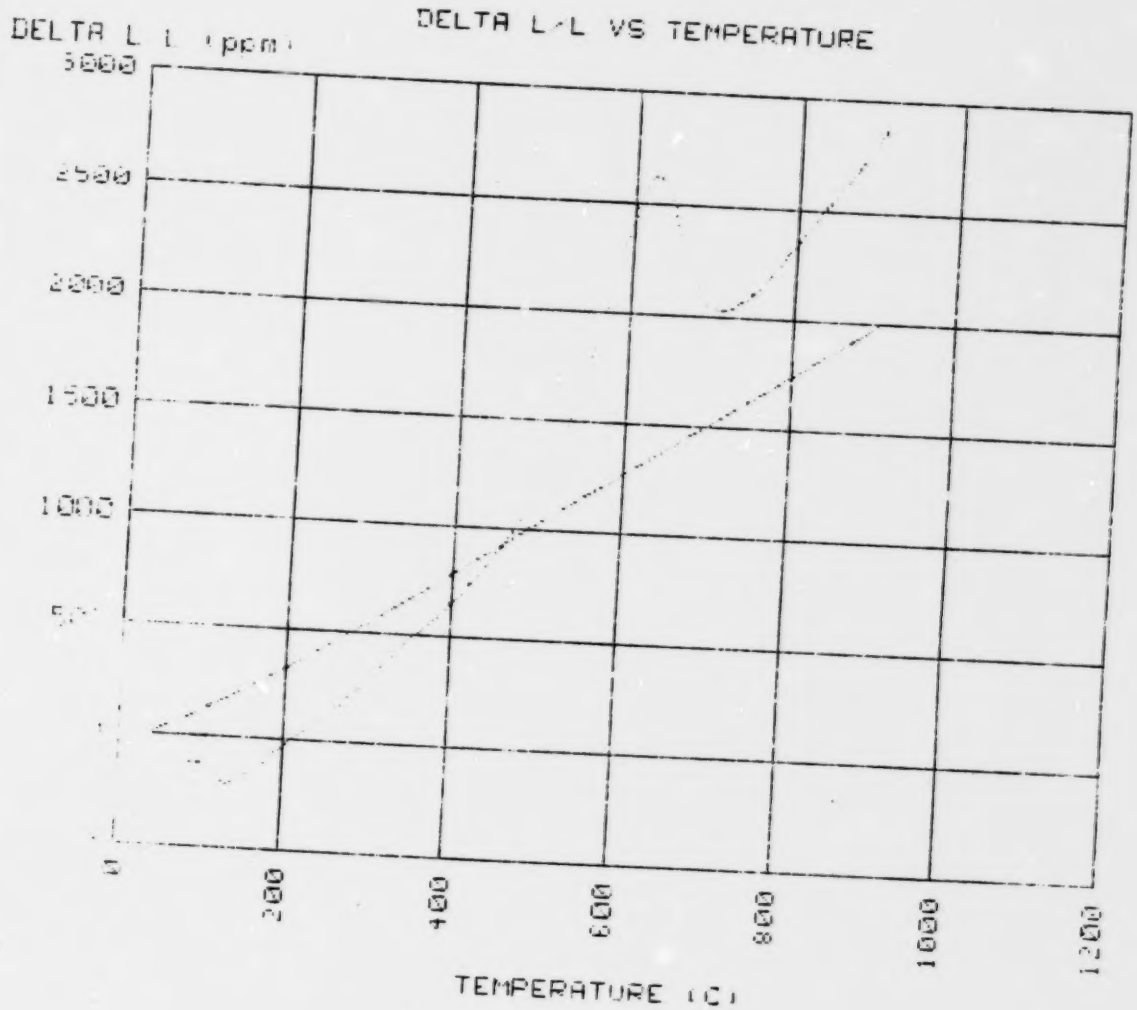
FIG. 18: Fly Ash - Thermal Expansion

Date: 26:07:16:40:28 Sample: A23 FA-1



Softening Point: 640°C

Fig. 19 Hot MOR of DA Compositions

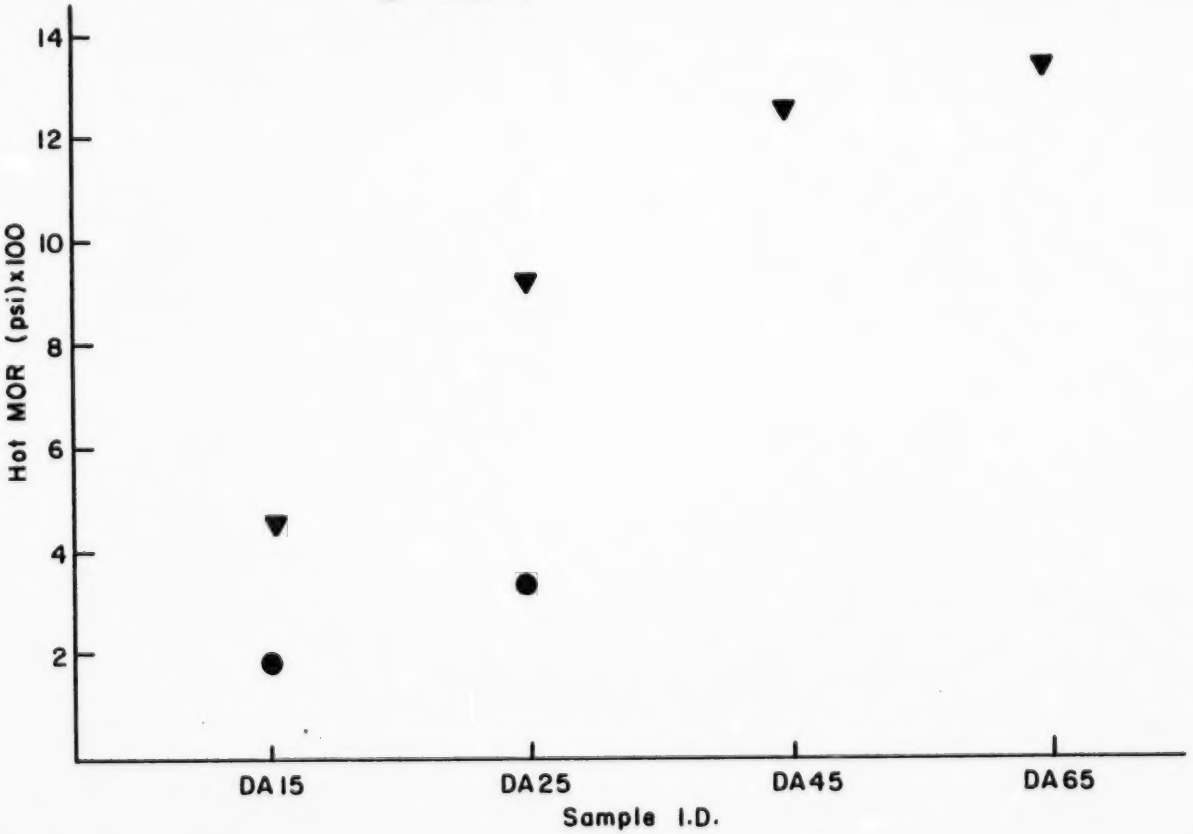


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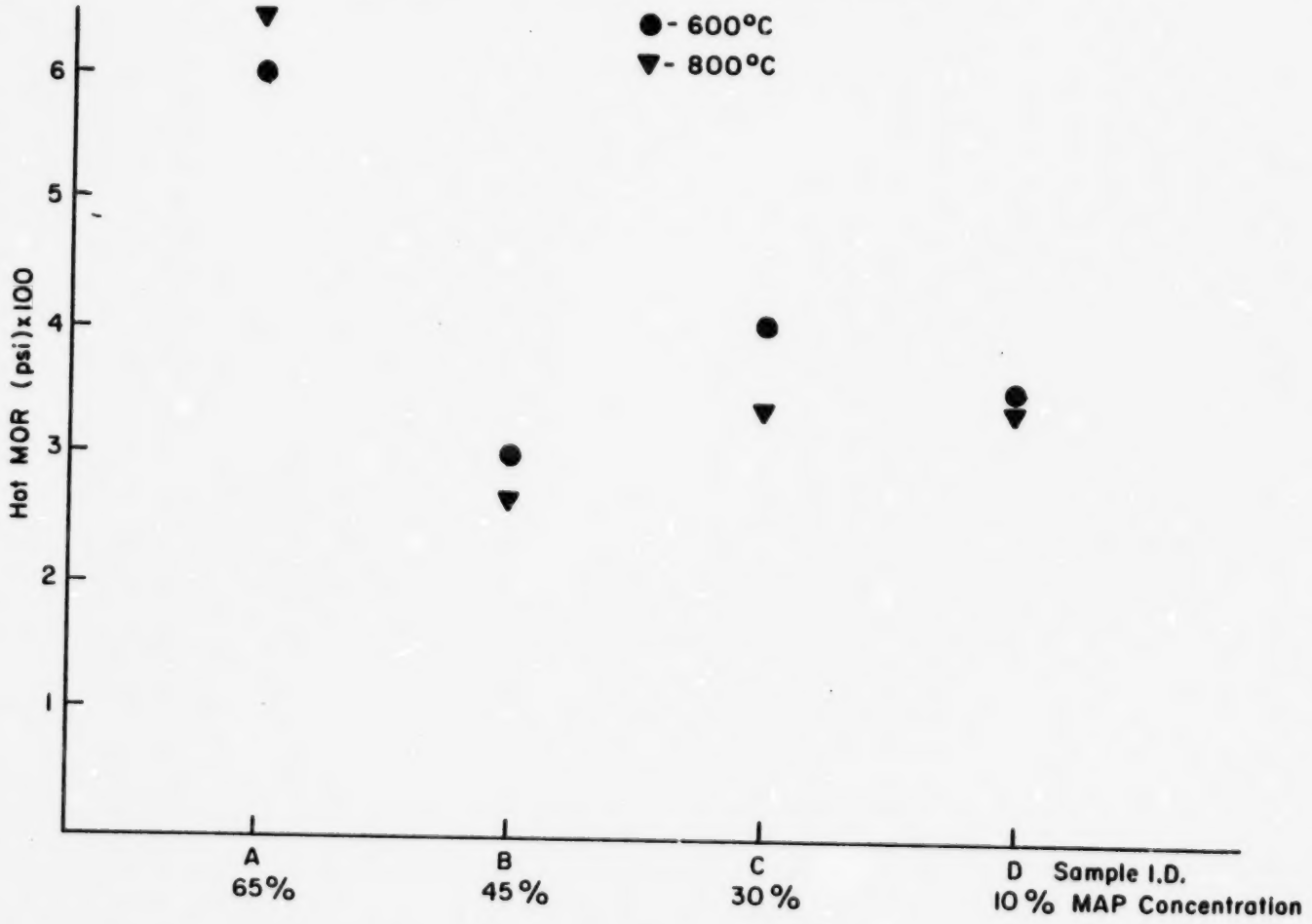
Fig. 20 Hot MOR of Fumed Silica Samples



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2. Drying in a controlled drying tunnel slightly improved the strength of the ceramic shell molds.

3. Samples dewaxed at high temperatures (~300°C, 1 hr) possessed high green or partially-fired strength. The strengths of these specimens were comparable to those of samples fired at 600°C for 1 hour (Fig. 14). This indicated that formation of a phosphate bonding phase occurred at a temperature below 300°C. Higher firing temperature may not be necessary except to remove the wax residue.

4. Facecoats using testing slurries were rejected due to the reaction between phosphate binder and pattern wax which formed porous and rough inner surfaces. Facecoats for all specimens were successfully prepared from SP 30 colloidal silica/zircon sand without any observable mismatch in thermal expansions on a quantitative basis.

5. For zircon/fused silica slurry with high MAP concentrations (70%), test strips warped during the firing process whereas samples with low MAP content (30%) dried very quickly before stuccoing. The optimum MAP concentration range is about 45-65% vol.

6. Specimens stuccoed with MgO exhibited exceptionally high green strength, especially with MGP at high concentration. However, fired strength of MgO samples (fired at 600°C, 1 hr) were poor as shown in Figs. 12 and 13.

7. For both MAP and MGP binders, shell molds stuccoed with Molochite had high fired strength although green strength was very soft and weak (Figs. 12 and 14).

8. Fumed silica samples possessed low green and fired strengths as compared to standard DPC specimens (Fig. 16).

9. Fly ash shell molds had exceptionally high strength and stable configuration but fly ash strips warped during firing. The cold MOR of fly ash strips was also lower than that of standard DPC samples (Fig. 15).

2.4.2 Improvement of the Process

The most promising compositions were the slurries of zircon/fused silica refractories with MAP concentrations of about 40-65% and with MGP concentration of about 40-70% (Table 5). A new set of MAP slurries was prepared and evaluated in order to improve the slurry compositions as well as the process parameters. The results of this investigation are shown in Figs. 21 and 22.

The green strength of these samples was greatly improved by drying in a controlled atmosphere of ammonia (Fig. 22). However, samples dried in the ammonia atmosphere had lower fired strength than the strips prepared in normal atmosphere conditions. (See Appendix A2 for Experimental Data) Further work is required to improve both green and fired strength of the ceramic shell molds for aluminum casting.

2.5 Metal Pouring Trial

This task was completed at DPC and is reported in DPC Final Report.

2.6 Other Completed Tasks

A brief literature review on phosphate bonding technology was prepared to obtain some fundamental background on phosphate bonding in ceramic refractories. This literature study (see Appendix A1) showed that phosphate bonding technology, especially MAP and MGP, has not been used in the investment casting industries.

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Assistant Research Scientist

G. Gowda

TABLE 5: Promising Slurries

Slurry I.D.	Refractories Zircon (g)	Refractories Fused Silica (g)	Binder (ml)	Water (ml)	Viscosity (sec) (Zahn Cup # 5)	Chemical Additives
DA45	2820	1880	MAP 675	855	11	5 ml ultra wet + 7 ml H_2O
DA65	2580	1720	MAP 975	555	11	"
BEM2	1780	1167	MGP 700	300	16	10 ml anti-foam, 5 ml ultrawet 60 ml H_2O
BEM3	1930	1287	MGP 500	500	16	"

Fig. 21 DA Compositions

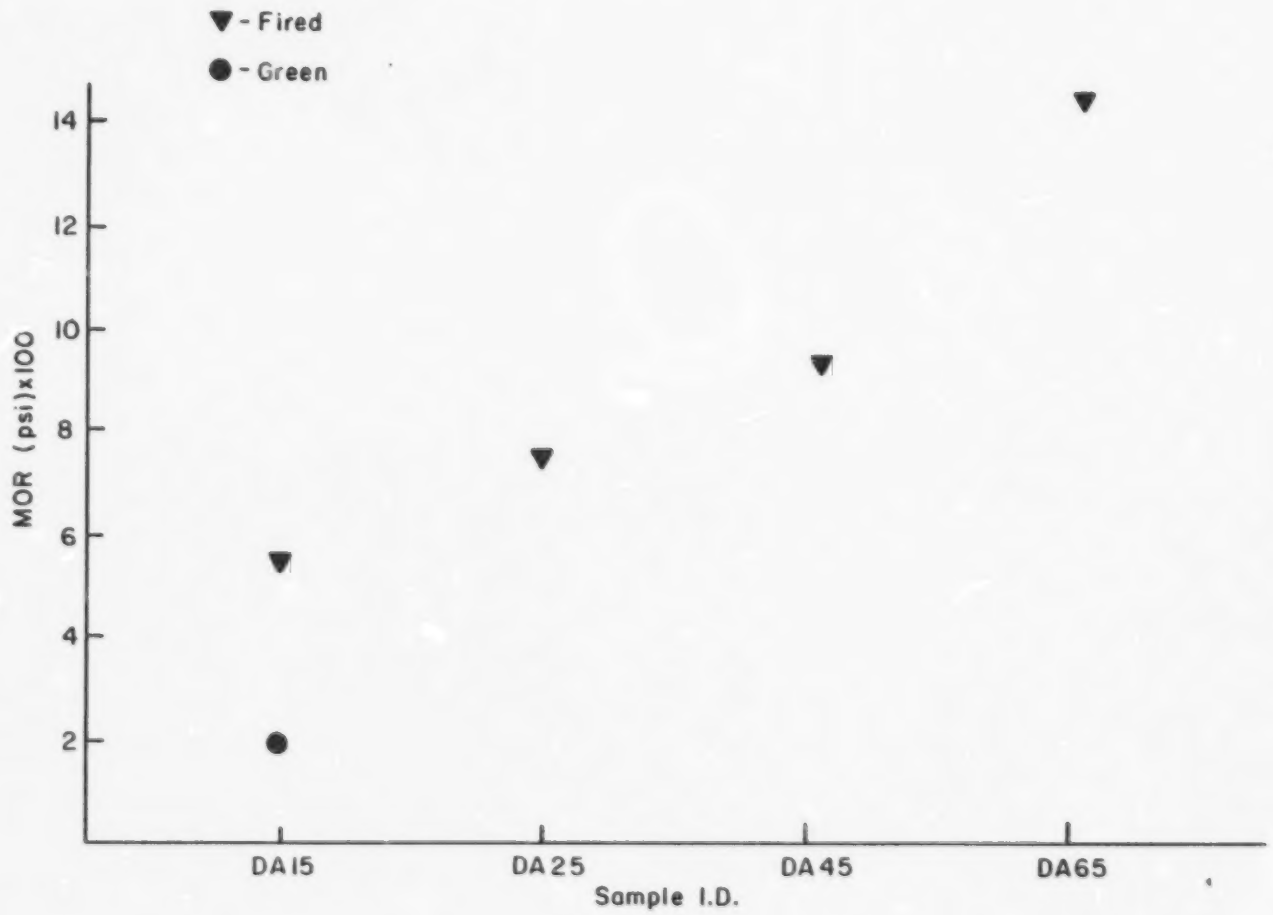

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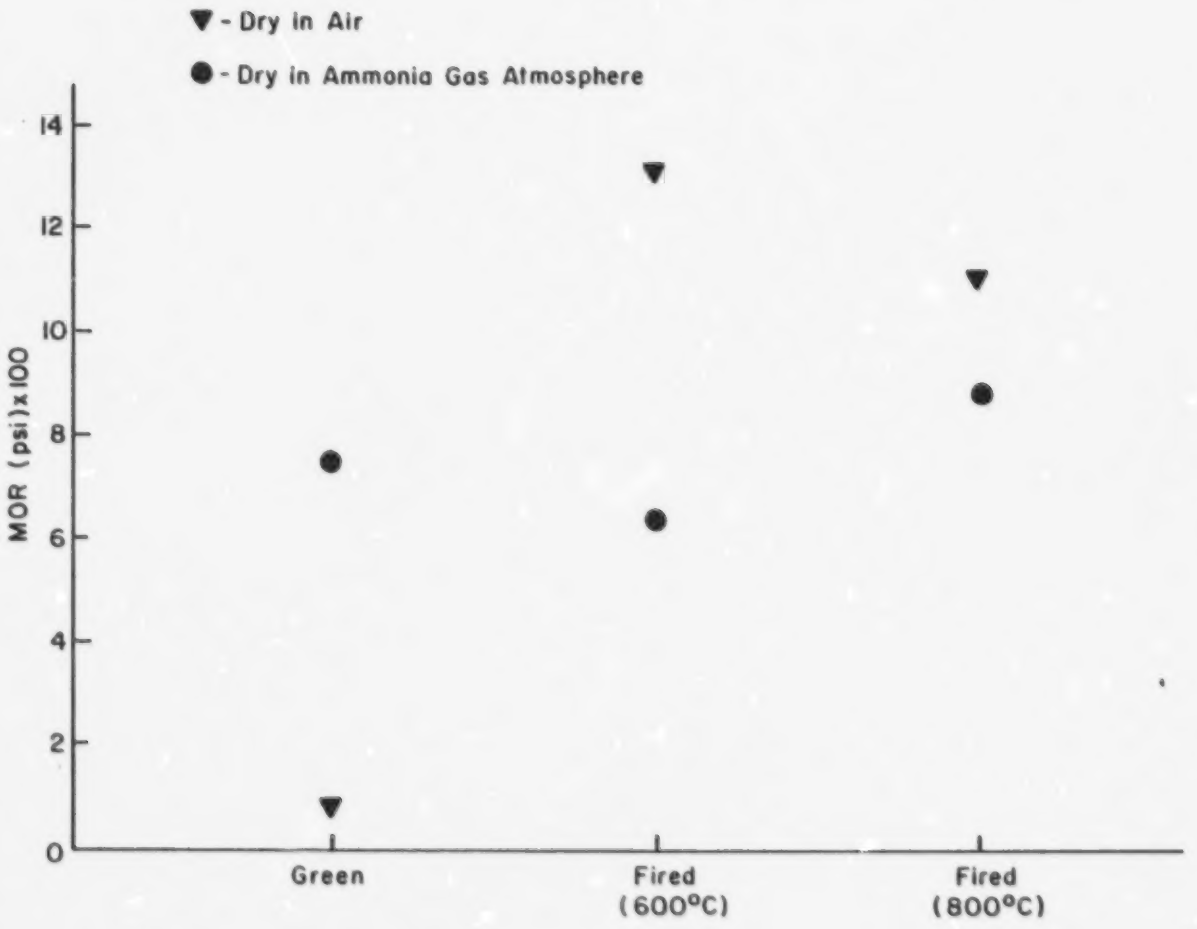
Fig. 22 Improvement of Green Strength (DA 45 Composition)



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APPENDIX A1

Phosphate Binder in Ceramic Refractory

A brief review

Prepared by
D. Nguyen

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1. INTRODUCTION

It has been known for may years that high temperature service ceramics can be prepared at a low firing temperature with a suitable binding agent. This offered significant energy saving by eliminating the need for high temperature processing.

Recently, new advanced products are available that produce phosphate-bonds in ceramic refractories, resulting in high strength articles. Phosphate bonds provide a strong bond over the temperature range of about 400-1500^{o}C where other bonding agents tend to weaken. In addition, the phosphate bond is not easily wetted by the molten metals in contact with it. Numerous processes both on heat-setting and cold-setting have been patented. Phosphate-bonds are of particular interest because of the high fusion temperature of many phosphates.

Despite the wide application in many ceramic processes, phosphate bonding technology has not been very popular in investment casting industries.

2. PHOSPHATE BONDING

2.1 General Chemistry

In 1950, Kingery [1,2] studied the use of phosphate bonds in ceramic materials. He stated that the phosphate bond is accomplished by three methods;

(i) The reaction between siliceous materials and phosphoric acid,

(ii) The direct addition or formation of acid phosphates,

(iii) The reaction between oxide and phosphoric acid.

The reaction of siliceous compounds with phosphoric acid results in a hard or translucent product. In addition to these bonding methods, ammonium phosphate, chromium-aluminum phosphate, alkali metaphosphate, magnesium acid phosphate, aluminum chlorophosphate hydrate and urea phosphate are also mentioned.

Phosphoric acid and Mono-aluminum phosphate (MAP) are the most frequently used. However, phosphoric acid and MAP tended to react too fast, as reported by several authors[3,4].

2.2 Phosphoric Acid

Phosphoric acid has been found to be a good bonding agent for high-alumina refractory. Phosphoric acid was used in zircon ($ZrSiO_4$) refractories with an alkaline, alkaline earth or magnesium zirconium silicate[5]. Phosphoric acid produced the best bonding result with the presence of siliceous materials. This may be due to the greater reactivity with the silicate component and the higher viscosity of the melts.

Aluminum, chromium and magnesium oxides[6,7] are also known to form strong bonds with phosphoric acid at 200°C. Aluminum hydrate may be used with refractory clay filler and phosphoric acid to form a bond that became permanent when heated from 100°C to 300°C[8].

Yutina[9] et al. reported on some phases formed by reaction of phosphoric acid with alumina. Hardening systems based on H_3PO_4 and TiO_2, CaO, FeO, Te_2O_3, NiO, ZnO, ZnO_2, MgO and CrO_3 have also been investigated. These authors concluded that phases formed when H_3PO_4 reacts with Al_2O_3 and with $Al(OH)_3$ are similar. Acid phosphate of the type $Al(H_2PO_4)_3$ is formed initially. Subsequent heating in the presence of excess Al_2O_3 produces a final bonding phase which is almost certainly $AlPO_4$[10].

Figure 1 based on studies reported by several investigators [11-16] show phase conversions in an aluminum phosphate binder with a molar ratio of P_2O_5/Al_2O_3 as 2.3.

Direct Calorimetric Analysis (DCA) studies by O'Hara et al.[10] showed that the bonding of the reaction Al_2O_3 and H_3PO_4 begins at ≈127°C. Most of the reactions occur over the range of 127-427°C involving the formation of aluminum phosphate and possible formation and melting of pyrophosphoric acid. They also found that phosphate-bonded alumina bodies fired to 2000°F (1090°C) have a lower room temperature strength than specimens cured to 700°F (370°C) or fired to 1500°F (815°C). Strength and stability of phosphate-bonded aluminum refractories can be enhanced through the use of chromic acid as partial replacement of phosphoric acid.

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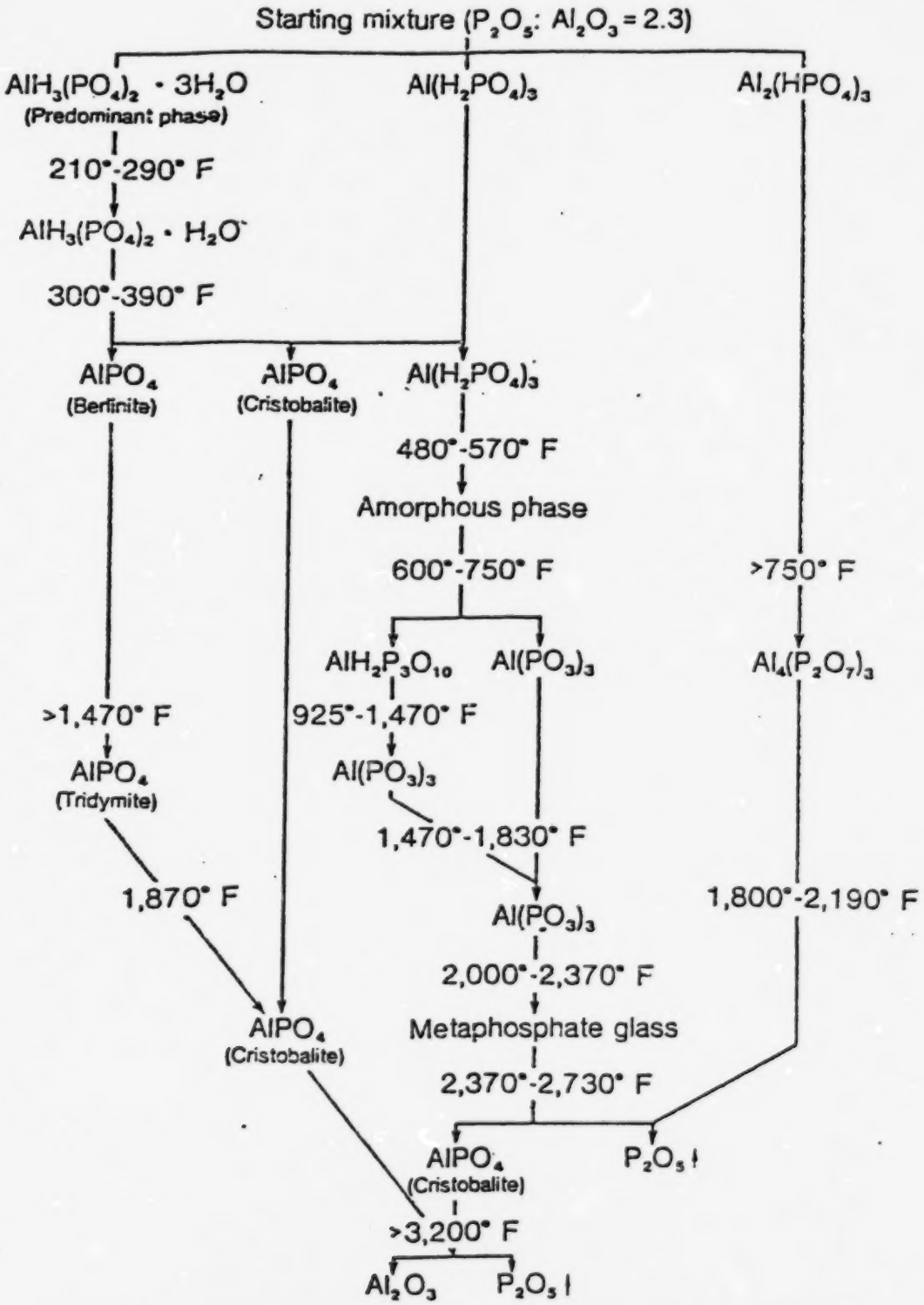

FIGURE : Effect of heat treatment on phase constitution of aluminum phosphate binder.

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Lyons et al.[17] found that phosphate-bonded high-alumina refractory composition are often faced with premature hardening and loss of workability.

The reaction of phosphoric acid with aluminum are believed to be as follows[18]:

$$Al_2O_3 + 6H_3PO_4 \longrightarrow 2Al(H_2PO_4) + 6H_2O \quad (1)$$

$$Al(H_2PO_4)_3 \rightleftharpoons AlPO_4 \cdot xH_2O + 2H_3PO_4 \quad (2)$$

$$2Al(H_2PO_4)_3 \xrightarrow{257^\circ C} Al_2(H_2P_2O_7)_3 + 3H_2O \quad (3)$$

$$xAl_2(H_2P_2O_7)_3 \xrightarrow{500^\circ C} \left(Al(PO_3)_3\right)_x + 3/2\ xH_2O \quad (4)$$

The $Al(H_2PO_4)_3$ is water soluble and is the bonding material in phosphated-bonded, high-alumina refractories. If the reaction proceeds as indicated in equation(2), the formation of $Al(PO_4 \cdot xH_2O)$ will result in the premature hardening of the mixture and the loss of workability. Therefore to improve the workability and increase storage life of the mixes, reaction(2)must be stopped or retarded to maintain the aluminum in the solution while preventing the formation of $AlPO_4 \cdot xH_2O$. Chemical agents such as 2 percent 5-sulphosalicylic acid acetyacetone, dextrin were introduced to accomplish this purpose[4].

The reactions of several oxides with phosphoric acid are listed in Table 1.

In the manufacture of high-alumina brick, Lyon[17] et al. found that it is necessary to prepare the mixtures of dry refractory materials and phosphatic acid several hours prior to pressing into shapes. This permits the phosphoric

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TABLE 1. - Oxide reactions with phosphoric acid (1,2)

Oxide	Time of setting, hours	Temp. rise of 0.5 cm^3, ° C	Modulus of rupture, psi	Product reported in chemical literature	Other data and observations
BeO	1/30	15	750	$Be(H_2PO_4)_2$; $Be(H_2PO_4)_2 \cdot BeHPO_4$	Normal reaction.
$Be(OH)_2$	1/30	18	570	.....do.....	Do.
MgO	NS	30	ND	$MgHPO_4$; $Mg(H_2PO_4)_2$	Violent reaction.
$Mg(OH)_2$	NS	ND	ND	.....do.....	Do.
MgO calcined at 1,280° C.	1/30	25	300	.....do.....	X-ray pattern shows MgO and weak lines for $Mg(H_2PO_4)_2$.
CaO calcined at 1,100° C.	NS	ND	ND	$Ca(H_2PO_4)_2 \cdot xH_2O$.....	Violent reaction.
CaO calcined at 1,100° C; liquid contained 9.6 pct CaO.	12	24	520	.....do.....	X-ray diffraction shows crystalline pattern.
SrO calcined at 1,400° C; liquid contained 9 pct SrO.	NS	0	ND	None.....	Violent reaction.
BaO calcined at 1,400° C; liquid contained 9 pct BaO.	NS	0	ND	.....do.....	Do.
CuO	3	6	570	$CuHPO_4 \cdot H_2O$.....	Normal reaction...
CdO	1/2	15	700	$Cd(H_2PO_4)_2$.....	X-ray pattern shows absence of crystalline $Cd_3(PO_4)_2$.
ZnO calcined at 1,100° C.	1/20	27	850	$ZnHPO_4 \cdot 3H_2O$.....	X-ray pattern shows absence of crystalline $Zn_3(PO_4)_2$. 0.0, 2, $4H_2O$.
SnO	3	3	100	$SnHPO_4$.....	None.
SnO_2	NR	0	ND	None.....	Do.
HgO	NS	23	ND	$Hg_3(PO_4)_2$.....	X-ray pattern shows $Hg_3(PO_4)_2$.
Hg_2O	NS	24	ND	Hg_3PO_4.....	X-ray pattern shows Hg_3PO_4.
NiO	NR	0	ND	None.....	None.
PbO	NS	7	ND	$Pb_3(PO_4)_2$.....	X-ray pattern shows $Pb_3(PO_4)_2$.
PbO_2	NR	0	ND	None.....	None.
Pb_3O_4	1/60	38	ND	$Pb(H_2PO_4)_4$	Cracked on setting; X-ray pattern shows crystalline product containing $Pb_3(PO_4)_2$; PbO_2 absent.
B_2O_3	NS	5	ND	H_2BO_3.....	None.
Al_2O_3	NR	0	ND	None.....	Do.
$Al_2O_3 \cdot xH_2O$	24	1	1,260	$Al(H_2PO_4)_3$.....	X-ray pattern shows amorphous product.
Co_2O_3	NR	0	ND	None.....	None.
$Cr_2O_3 \cdot xH_2O$	NR	0	ND	.....do.....	Do.
Fe_2O_3	72	2	ND	$FeH_3(PO_4)_2 \cdot 2\text{-}1/2H_2O$; $Fe(H_2PO_4)_3$.	Tacky product.
Fe_3O_4	1/60	36	300	None.....	None.
La_2O_3	1/40	36	ND	$La_2(HPO_4)_3$.....	Violent reaction.
La_2O_3 calcined at 1,400° C.	1/6	18	400	.....do.....	None.
Y_2O_3	1/30	30	ND	$Y_2(HPO_4)_3$.....	Shrinkage cracking.
SiO_2	NR	0	ND	None.....	None.
H_2SiO_3	NR	0	ND	.....do.....	Do.
TiO_2	NR	0	ND	.....do.....	Do.
$Ti(OH)_4$	12	2	200	$TiOHPO_4$.....	Do.
ZrO_2	NR	0	ND	None.....	Do.
$Zr(OH)_4$	18	5	250	$Zr(HPO_4)_2$.....	Do.
ThO_2 from $Th(NO_3)_4$ at 300° C.	48	2	ND	$Th(HPO_4)_2 \cdot H_2O$.....	Tacky product.
CeO_2	NR	0	ND	None.....	None.
V_2O_5	1/6	30	180	$VO_2H_2PO_4 \cdot 4\text{-}1/2H_2O$...	Do.
$CrO_3 \cdot xH_2O$; MoO_3; $WO_3 \cdot xH_2O$.	NR	0	ND	None.....	Do.

ND Not determined.
NR No reaction.
NS Not set.

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acid to react with the alumina compound of the mix to produce the bonding material aluminum acid phosphate. Without this aging, the bricks tend to crack during the drying stages. Oxalic acid was also used as an inhibitor which prevents the formation of insoluble aluminum phosphate.

Sheets et al.[19] used phosphoric acid to produce castable refractories. 1% of Rodine 78, a complex amine, was used to prevent bloating. The authors also confirmed the statement of Gitzen[20] et al., that a higher-strength bond can be obtained by bonding alumina with phosphoric acid rather than aluminum phosphate as the bonding agent.

Phosphoric acid when heated reacted with alumina and silica as studied by West and Veale[21]. They used this reaction to produce phosphate-bonded silica brick.

Gilham-Dayton[22] investigated the use of phosphoric acid and aluminum acid phosphate as the bonding agents in silica, Molochite and Mullite mixes. Cold crushing strength of Mullite bonded with $Al(H_2PO_4)$ was found to be stronger than with phosphoric acid as shown in Tables 2 and 3.

Rigby[23] studied the application of phosphoric acid and hydrated alumina and several bonding agents in high-alumina refractories. He found that phosphoric acid with 1.75 specific gravity must be used in conjunction with

Table 2 (22)

Silica bonded with Phosphates

	Firing temperature (°C)	Cold-crushing strength (lb/in²)	Apparent porosity (%)	Specific gravity (g/ml)	Permanent linear change on firing (%)	P_2O_5 found (%)
Silica fines bonded with H_3PO_4 (Si1)	400	2,500	36·3	2·65	N.D.	6·0
	500	2,900	36·4	2·65	0	6·0
	700	1,200	37·2	2·63	+0·1	6·2
	900	2,000	37·2	2·63	+0·3	5·9
	1,100	9,700	30·3	2·56	−1·5	5·6
	1,300	6,100	25·9	2 49	−2·6	5·5
	1,500	N.D.	21·3	2·31	N.D.	5·7
Silica bonded with H_3PO_4 (Si2)	400	2,200	20·8		0	
	1,300	3,100	18·1		+1·0	
	1,500	N.D.	26·1		~+4·0	
Silica fines bonded with $Al(H_2PO_4)_3$ solution (Si3)	105	2,700				
	300–450	Samples collapsed in air owing to absorption of moisture				
	500	2,700	37·2	2·63	0	
	700	1,100	38·3	2·63	+6·7	
	900	1,200	38·2	2·63	+0·5	
	1,100	3,500	35·6	2·60	−0·3	
	1,300	2,500	34·1	2·54	−0·3	
	1,400	N.D.	34·4	2·45	+1·6	
	1,500	3,200	34·4	2·34	+2·4	

Table 3 (22)

Mullite bonded with Phosphates

	Firing temperature (°C)	Cold crushing-strength (lb/in²)	Apparent porosity (%)	Bulk density (g/ml)	Permanent linear change on firing (%)
C1. Mullite bonded with $Al(H_2PO_4)$ solution	120	4,100	n.d.	n.d.	
	250	4,700	n.d.	n.d.	
	500	4,200	23·4	2·39	
	750	4,700	n.d.	n.d.	
	1,000	5,000	22·9	2·40	
	1,250	6,500	22·8	2·41	−0·1
	1,400	7,400	22·2	2·43	−0·3
	1,600	n.d.	21·2	2·5	−0·9
	1,700	n.d.	18·8	2·5	−1·3
C2. Mullite bonded with ball clay and H_3PO_4	120	2,500			
	250	3,200			
	500	4,100			
	750	4,400			
	1,000	4,300			
	1,250	6,700			

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hydrated alumina, since the specimens utilizing phosphoric acid alone were too fragile to handle.

Experience at ORF and ceramic companies has found phosphoric acid bonding with alumina batch additions at times tends to be inconsistent in larger pieces. A high reject rate cannot be tolerated and the consistency obtained in the laboratory cannot always be achieved in production situations.

2.3 Aluminum Acid Phosphate

A second method of using phosphates in refractory chemical bond formation is by the direct addition of acid phosphates.

The most important characteristic of a liquid binding agent is the acidity which is defined as x, the molar P_2O_5: Al_2O_3 ratio[3]. It has been shown that mixtures with $x < 3$ are metastable. Mixtures in which $x = 2.3$ precipitate and harden on prolonged storage and mixtures <2.3 are even more unstable.

Typical commercial products have $x = 3$ and are about 50%w/w solution of $Al(H_2PO_4)_3$. Kolb[24] found that when pure $AlPO_4$ (cristobalite structure) was heated to about 1500°C, it began to decompose liberating P_2O_5 as shown in Table 4.

Boule and D'Yuoire[25] studied the effect of heat on $Al(H_2PO_4)_3$ and showed that over the temperature range 100°C-500°C water is gradually lost and the product is mainly amorphous until about 500°C when aluminum metaphosphate is found.

TABLE 4

Thermal Stability of $A\ell PO_4$ in Air[24]

Temp./°C	Duration/hr	Composition %	
		$A\ell PO_4$	$A\ell_2O_3$
1500	1	93.7	6.3
1650	1 —	86.8	13.2
1800	1	86.5	13.5
2200	not stated	-	100.00

Kingery[26] also showed that $A\ell(H_2PO_4)_3$ solution, like all soluble salts, tends to migrate to the surface of the refractory during drying and also the concentration of the phosphate is greater towards the surface of the refractory and the outer layers tend to be stronger than the interior. An aluminum phosphate-bonded refractory composition was patented in 1973[27]. This process provided a composition containing an aluminum phosphate bonding solution for making ceramic refractory shapes and such composition can be cast and hardened in situ without heating.

The preferred concentration of phosphate solution is that to produce a specific gravity of 1.12 to 1.15 with P_2O_5 and $A\ell_2O_3$ content as follows:

TABLE 5

Phosphate Composition[27]

Phosphate Solution	Specific Gravity of 1.12	1.25	1.50
P_2O_5 content			
Wt % (typical)	3.0	16.0	32.0
g/cc (typical)	0.103	0.203	0.406
Al_2O_3 content			
Wt % (typical)	2.2	4.3	8.3
g/cc (typical)	0.027	0.054	0.108

Suitable ceramic grain materials include alumina, mullite, zirconia, magnesium aluminates, beryllia, cordierite, dumorterite and pyrophyllite. Preferred ceramic materials are alumina, mullite and zirconia. Foessil and Treffer[6] used phosphate bonding in MgO refractories. They noted that the reaction between magnesia and phosphoric acid or acid phosphate is usually quite violent. They developed a new phosphate-containing basic refractory composition using sodium phosphate polymer as the inert binder. The phosphate bonding results in significantly higher hot strength than conventional bonding as shown in Figure 2[6],

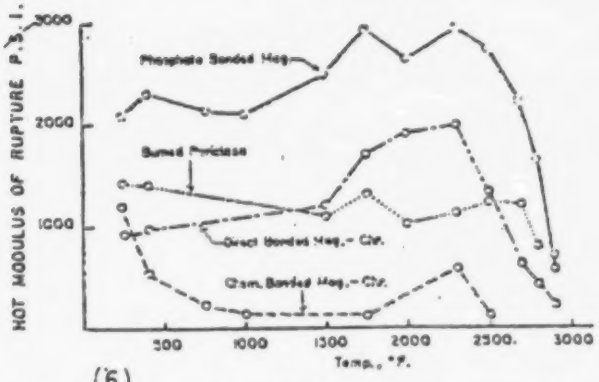


Fig. 2 [6] Continuous hot modulus test of basic refractory brick.

Fisher[28] studied the bonding of alumina powder using various bonding agents. He found that phosphate produced the strongest refractories and strength increase with increasing acidity.

The cements investigated are ammonium phosphate, mono-aluminum phosphate, aluminum mono-acetate and ethyl silicate. The characteristics of the phosphate bond are;

(i) Effective curing takes place at 100°C-200°C

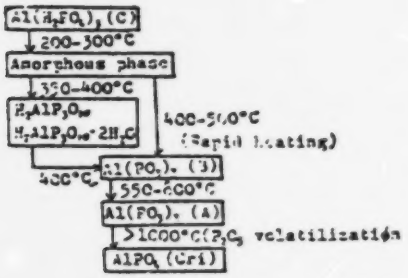
(ii) Strength increase with firing temperature at about 400°C above which a loss in strength occurs.

The phosphate bonded material showed excellent dimension stability up to 1000°C.

The reaction of MgO and aluminum acid phosphate has been studied[29]. Various systems were investigated in which the molar P: (Al+Mg) ratio was varied using a reagent grade MgO, monoaluminum phosphate and aluminum hydroxide. As the amount of MgO increased, so the rate of setting time increased. The reaction was endothermic and the heat of reaction increased with the magnesia content. The main reaction is represented by equation (5);

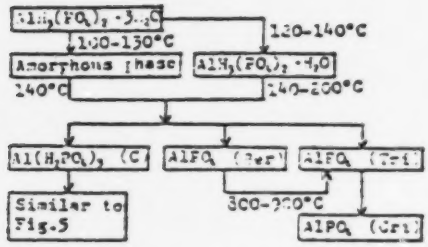
$$Al(H_2PO_4)_3 + m\,MgO + (1-m/2)Al_2O_3 + KH_2O - m(MgPO_4,3H_2O) + (3-m)(AlPO_4,nH_2O) \quad (m \leq 2) \qquad (5)$$

Thus, $MgHPO_4,3H_2O$ is formed as a crystalline salt. Some gel-like $AlH_3(PO_4)_2 3H_2O$ is also found. Attempts to form a cold setting system in which P: (Al+ Mg) ratio was greater than 1 failed due to the formation of water soluble $Mg(H_2PO_4)_2$. On heating, the phosphate changed to an amorphous material and then to $Al(PO_3)_3$ type B above 480°C and type A above 550°C (Figures 3 and 4).



(29)

Fig.3 Thermal change of $Al(H_2PO_4)_3$ (form C).



(29)

Fig. 4 Thermal change of $AlH_3(PO_4)_2 \cdot 3H_2O$.

2.4 Other Phosphate Bonds

The use of alkali metaphosphate as chemical bonding agents in refractories has been studied[30]. Sodium hexametaphosphate ($Na_6P_6O_{18}$) forms rubber-like polymers and yields high-strength ceramics with fire-clay aggregates. Lime et al.[31] described the use of complex P_2O_5-containing ammonium phosphate solution in combination with magnesia for bonding various refractory aggregates. Improved hot strengths and good adherence to slagged surfaces are advantages over conventional bonds.

Foessil and Treffer[6] used sodium polyphosphate in basic refractories. They showed that very high hot strengths of 1500-2500 psi could be achieved at $\simeq 1482^{o}C$ in magnesite and magnesite chrome refractories under certain conditions.

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Venable and Treffer[32] studied the structure and phase formation of sodium polyphosphate compounds using X-ray diffraction technique. They found that the bonding phase is $CaNaPO_4$, sodium rhenanite.

The use of magnesium phosphate, ammonium phosphate was also reported by Gilham-Dayton[22]. He found that setting time for chrome magnesite and magnesite increases in the order of;

$$H_3PO_4 < Mg(H_2PO_4)_2 < Al(H_2PO_4)_3 < NH_4H_2PO_4$$

Castable refractories can be produced from this method. The chemistry of sodium phosphate bonding with magnesium oxide refractory was investigated by Lyon et al.[17]. The reactions were as follows:

$$2NaPO_3 + H_2O \rightarrow 2NaH_2PO_4 \quad (6)$$

$$2NaH_2PO_4 + MgO + H_2O \rightarrow Mg(H_2PO_4)_2 + 2NaOH \quad (7)$$

$$Mg(H_2PO_4)_2 + MgO \rightarrow 2MgHPO_4 \quad (8)$$

$$x\ Mg(H_2PO_4)_2 \xrightarrow{\text{heat}} (Mg(PO_3)_2)x$$

$$2MgHPO_4 \xrightarrow{\text{heat}} Mg_2P_2O_7$$

They also found that to effectively bond MgO with phosphate, it is necessary for the bonding materials to be water soluble and to be essential non-reactive with MgO at room temperature.

Magnesium phosphate solution was used as liquid binder on mixing cement as reported by Sudakas[33]. He noted that the addition of magnesium oxide to concentrated (75.0%) phosphoric acid increase the strength of the specimens after setting.

Chvatal[34] has developed a binder system based on colloidal solution of $Al_2O_3.3P_2O5.xCr_2O_3$ where x varies from 0.1 to 1.0. These phosphate bonds are more thermally stable than condensed aluminum phosphate.

Aluminum chlorophosphate hydrate has also been developed as ceramic binder[35,36]. This chemical is a dry powder highly soluble in water and decomposes on heating to form $AlPO_4$ without forming intermediate metaphosphate. It can be used in both heat-setting and cold-setting formulation, (the latter by the addition of MgO). This binder has been modified[37] to include a small proportion of an acetylenic alconol condensate that enables the bond to be used in conjunction with aggregates containing metallic iron.

Binders comprising both aluminum phosphate and ammonium or urea phosphate have also found use in heat-setting high alumina compositionswhere a dry powder is required[38].

3. PROPERTIES OF PHOSPHATE BONDS

With proper selection of bonding material and optimum size distribution of material, phosphate-bonded articles exhibit high strength upon heating. They possess high refractory strength and good abrasion resistance after heating (Fig.5).

Phosphoric acid or monoaluminum phosphate solution is used in preparing unfired refractory brick. Pressed bricks composed of high alumina aggregate containing 5 to 10wt% of the phosphate bonding agent, need only to be cured at moderate temperature.

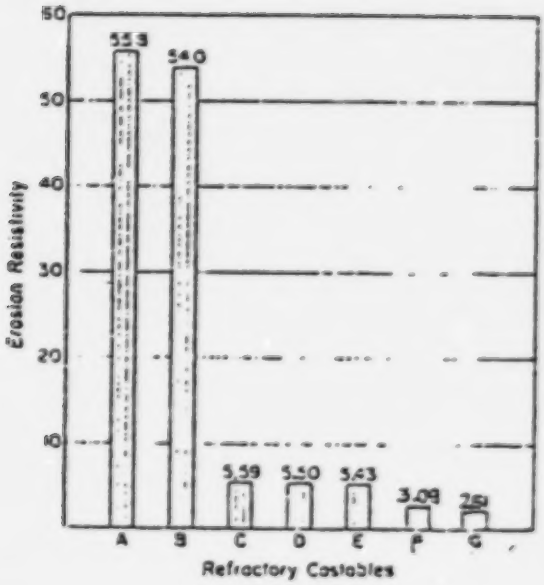

Figure 5[20] Erosion Resistivity of Refractory Castable
A and B-Aluminum-Phosphate Bonded
C-G—Commercial Castable

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These products have high cold crushing strength, accurate dimensional stability and good slag and abrasion resistance properties that have made them acceptable for use in electric arc furnace roofs (Fig. 6 and 7).

The properties of phosphated-bond brick and other refractory bricks are shown in Tables 6 and 7[39].

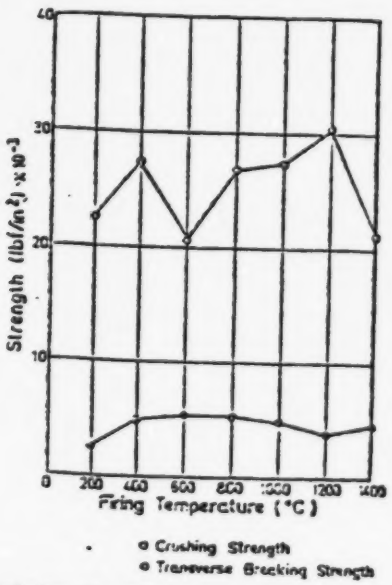

FIGURE 6 —Variation of cold strength with temperature for alumina-mono-aluminium phosphate compacts. (28)

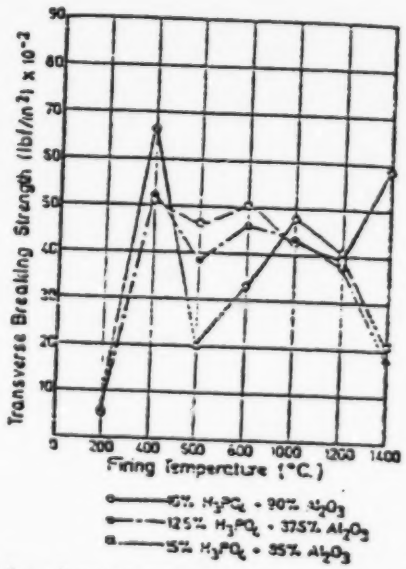

FIGURE 7 —Variation of cold-transverse-breaking strength with temperature for alumina-phosphoric acid compacts. (28)

Table 6 (39)

Typical Physical Properties of some Commonly Used and Trial Roof Refractories

	Silica	*85% Al_2O_3 fired*	*80–85% alumina phosph. bonded*	*96% Al_2O_3*	*High-fired mag-chrome*	*High strength magnesite*
Porosity (%)	19–23	17–21	15–19	13–17	16–20	13·5–17·5
Pores						
More than 40μ	0·4	0·5	0·1	0·7	1·0	1·3
More than 20μ	1·1	2·0	0·5	3·6	5·2	3·7
Thermal expansion (%) 0–1000°C	1·3	0·66	0·66	0·80	0·90	1·26
P.V.C. after 2hr at 1500°C	Nil to +1·0	Nil to −0·7		Nil	—	—
2hr at 1600°C	Nil to +1·0	Nil to −2·0	+1·5 to +3·5	Nil	Nil to +0·5	Nil
2hr at 1700°C	—	−1·0 to −3·0	+1·0 to −3·0	−0·2	Nil to +0·5	−0·4 to −0·6
Thermal conductivity (mean temp. 900°C)	12	11	11	18	17	36

Table 7 (39)

Typical Mechanical and Chemical Properties

	Silica	*85% Al_2O_3 fired*	*80–85% alumina phosph. bonded*	*96% Al_2O_3 (tabular)*	*High fired mag-chrome*	*High strength magnesite*
M.O.R. (p.s.i.)						
Room temp.	1300	1700	1200	3000	750	2650
1260°C	1100	2000	600	1000	1600	2450
1400°C	900	1000	350	600	1000	2400
1500°C	—	—	—	—	500	2000
1600°C	—	—	—	—	250	900
Creep in Torsion (mR/hr)						
1300°C	—	2–5	~100	—	6·5	0·7
1400°C	0·7	41	—	7·5	25·0	2·5
1500°C	—	—	—	—	—	5·0
Chem. analysis (%)						
SiO_2	96·5	8·5	11·0/8·2	2·70	1·9	1·7
TiO_2	0·1	2·7	2·7/2·6	0·04	—	—
Fe_2O_3	0·5	1·6	1·4/1·4	0·10	7·1	0·7
Al_2O_3	0·6	86·0	32·0/84·0	96·60	11·6	3·2
Cr_2O_3	—	—	—	—	13·0	—
CaO	1·7	0·4	0·3/0·3	0·02	1·0	2·9
MgO	0·1	0·1	0·2/0·2	0·02	65·0	94·2
Alkalis	0·15	0·2	0·3/0·3	0·30	—	—
P_2O_5	—	—	1·5/3·0	—	—	—
Cost/unit volume (silica = 1) standard shapes	1·0	2·7	2·6	10·2	2·8	3·9

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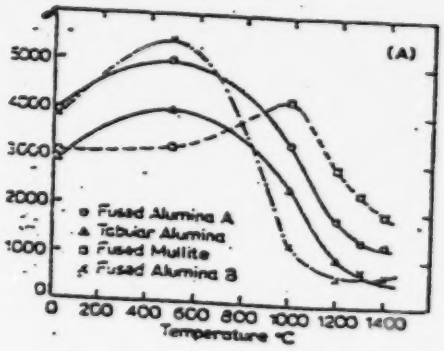
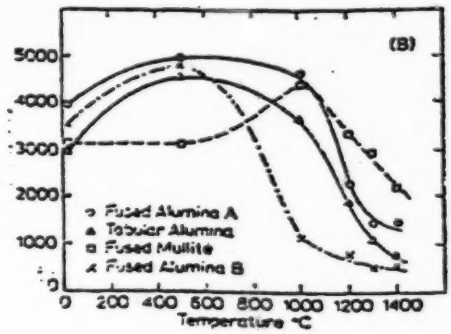
Palfreyman[40] investigated the hot strength properties of high-alumina refractories. He found that values of over 2,000 psi were obtained for the Modulus of Rupture of fused mullite specimens bonded with ground calcined alumina and phosphoric acid. Specimens bonded with calcined alumina and phosphoric acid have higher green densities than those with other binders and also have high hot MOR values (Fig.8 and 9).

The volume stability of brick is measured either by creep under load or by reheat-change at high temperature and is an important performance criterion in many refractories applications. The volume stability of fired and unfired phosphated-bonded high-Al_2O_3 brick was evaluated by Boab and Blackwood[41]. These authors concluded that phosphate-bonded materials would not be suitable in application where high temperature volume stability is a requirement (Tables 8 and 9).



(40)

Figure 8: Modulus of Rupture vs Temp. for specimens bonded with calcined alumina and phosphoric acid fired 1 hr at 1600°C.



(40)

Figure 9: Modulus of Rupture vs Temp. for specimens bonded with calcined alumina and phosphoric acid fired 1 hr at 1700°C

Table 8 Physical Properties of 85% Alumina Brick

Brand Classification	A-85 Conventionally made	B-85 Burned phosphate-bonded	C-85 Chemically bonded
Physical properties (avg. of 10 brick)			
Modulus of elasticity, (psi×10⁻⁴)	5.070	8.085	9.784
Modulus of rupture (psi)	1994	2967	1444
Apparent porosity (%)	19.2	18.6	16.5
Bulk density (g/cm³)	2.89	2.85	2.92
Apparent specific gravity	3.60	3.51	3.50
Reheat test, % linear change (2910°F, avg. of 3)	−0.77	−0.73	−1.77
Long-time load, % linear change (2600°F, 25 psi, 100 h)	−3.40	−4.69	−7.15

(41)

Table 9 Physical Properties of 90% Alumina Brick

Brand Classification	A-90 Conventionally made	B-90 Burned phosphate-bonded
Physical properties (avg. of 10 brick)		
Modulus of elasticity (psi×10⁻⁴)	6.887	7.579
Modulus of rupture (psi)	3082	3035
Apparent porosity (%)	16.7	17.1
Bulk density (g/cm³)	2.93	2.84
Apparent specific gravity	3.52	3.42
Reheat test, % linear change (2910°F, avg. of 3)	+0.30	−0.83
Long-time load, % linear change (2600°F, 25 psi, 100 h)	+0.16	−5.43

(41)

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Jackson and Partridge[39] compared the properties of various types of brick (including the phosphate-bonded high-alumina type) for electric arc furnace roofs. The phosphate-bond produced properties similar to those of the normal fired bricks, but has only 1/3 the hot MOR and failed in torsion at 1300°C. Phosphate-bonded silicon carbide refractories are used in steam generating boilers [42].

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APPENDIX A2

Experimental Data

TABLE 1

EXPERIMENTAL CERAMIC SHELLS

Date	Shell No.	Facecoat		Backup (1&2)		Backup (3&4)		Seal Coat	Dipping Characteristics	Drying Process: 2-3days	De-waxed Temp. (°C)	Cold MOR (Green) lb/in²	Cold MOR (Fired) lb/in²	Hot MOR (Fired) lb/in²	Firing Time & Temp.	Comments
		Slurry	Refr.	Slurry	Refr.	Slurry	Refr.									
5/5/83	BEA1A	SS1	Zircon Sand	BEA1	Mgo (30-80)	BEA1	(16-30) Mgo	BEA1	Dry very quickly	Air	140	860	-	-	-	Good sample
5/5/83	BEA1B	SS1	Zircon Sand	BEA1	Molochite (30-80)	BEA1	Molochite (16-30)	BEA1	Dry slowly	Air	140	-	1160	-	600°C 1 hr	Good sample
5/5/83	BEA1C	SS1	Zircon Sand	BEA1	Molochite (30-80)	BEA1	Molochite (16-30)	BEA1	Dry slowly	Drying Tunnel	140	-	1488	-	600°C 1 hr	Good sample
5/5/83	BEA1D	SS1	Zircon Sand	BEA1	Mgo (30-80)	BEA1	(16-30) Mgo	BEA1	Dry slowly	Air	300	535.4	-	-	-	Good sample
5/5/83	BEA1E	BEA1	Zircon Sand	BEA1	Molochite (30-80)	BEA1	(16-30) Molochite	BEA1	Dry very slowly	Air	300	1395	-	-	-	Porous and rough surface
5/5/83	BEA1F	SS1	Zircon Sand	BEA1	Molochite (30-80)	BEA1	Molochite (16-30)	BEA1	Dry slowly	Air	300	1691	-	-	-	Good sample
5/5/83	BEA1G	SS1	Zircon Sand	BEA1	Molochite (30-80)	BEA1	Molochite (16-30)	BEA1	Dry slowly	Drying Tunnel	300	1393	-	-	-	Good sample
5/5/83	BEA1H	SS1	Zircon Sand	BEA1	Mgo (30-80)	BEA1	Mgo (16-30)	BEA1	Dry slowly	Air	300	-	335	-	600°C 1 hr	Good sample
5/5/83	BEA1I	BEA1	Zircon Sand	BEA1	Molochite (30-80)	BEA1	Molochite (16-30)	BEA1	Dry slowly	Air	300	-	1590	-	600°C 1 hr	Porous surface
5/5/83	BEA1J	SS1	Zircon Sand	BEA1	Molochite (30-80)	BEA1	Molochite (16-30)	BEA1	Dry slowly	Air	300	-	1440	-	600°C 1 hr	Good sample
5/5/83	BEA1K	SS1	Zircon Sand	BEA1	Molochite (30-80)	BEA1	Molochite (16-20)	BEA1	Dry slowly	Drying Tunnel	300	-	1120	-	600°C 1 hr	Good sample

TABLE 2
EXPERIMENTAL CERAMIC SHELLS

Date	Shell No.	Facecoat		Backup (1&2)		Backup (3&4)		Seal Coat	Dipping Characteristics	Drying Process (2-3days)	De-waxed Temp. (°C)	Cold MOR (Green) lb/in^2	Cold MOR (Fired) lb/in^2	Hot MOR (Fired) lb/in^2	Firing Time & Temp.	Comments
		Slurry	Refr.	Slurry	Refr.	Slurry	Refr.									
5/5/83	BEA2A	SS1	Zircon Sand	BEA2	MgO (30-80)	BEA2	MgO (16-30)	BEA2	Dry very quickly between coats	Air	140	595	-	-	-	Good sample
5/5/83	BEA2B	SS1	Zircon Sand	BEA2	MgO (30-80)	BEA2	MgO (16-30)	BEA2	Dry very quickly between coats	Air	140	-	450	-	600°C 1 hr	Good
5/5/83	BEA2C	BEA2	Zircon Sand	BEA2	Molochite (30-80)	BEA2	Molochite (16-30)	BEA2	Dry very slow	Air	140	-	1530	-	600°C 1 hr	Rough, porous surface
5/5/83	BEA2D	SS1	Zircon Sand	BEA2	Molochite (30-80)	BEA2	Molochite (16-30)	BEA2	Dry slow	Air	140	-	2036	-	600°C 1 hr	Sample bended upon firing
5/5/83	BEA2E	SS1	Zircon Sand	BEA2	Molochite (30-80)	BEA2	Molochite (16-30)	BEA2	Dry slow	Drying Tunnel	140	Elasticity could not break	-	-	-	Good green sample
5/5/83	BEA2F	SS1	Zircon Sand	BEA2	MgO (30-80)	BEA2	MgO (16-30)	BEA2	Dry very quickly	Air	300	-	-	-	-	Good green sample
5/5/83	BEA2G	SS1	Zircon Sand	BEA2	MgO (30-80)	BEA2	MgO (16-30)	BEA2	Dry very quickly	Air	300	520	-	-	-	Good green sample
5/5/83	BEA2H	BEA2	Zircon Sand	BEA2	Molochite (30-80)	BEA2	Molochite (16-30)	BEA2	Dry very slowly	Air	300	950	-	-	-	Porous, rough surface
5/5/83	BEA2I	SS1	Zircon Sand	BEA2	Molochite (30-80)	BEA2	Molochite (16-30)	BEA2	Dry very slowly	Air	300	-	1585	-	600°C 1 hr	Sample bended upon firing
5/5/83	BEA2J	SS1	Zircon Sand	BEA2	Molochite (30-80)	BEA2	Molochite (16-30)	BEA2	Dry slowly	Air	300	-	2165	-	600°C 1 hr	Sample bended upon firing
5/5/83	BEA2K	SS1	Zircon Sand	BEA2	Molochite (30-80)	BEA2	Molochite (16-30)	BEA2	Dry slowly	Air	300	1791	-	-	-	Good sample
5/5/83	BEA2L	SS1	Zircon Sand	BEA2	Molochite (30-80)	BEA2	Molochite (16-30)	BEA2	Dry slowly	Drying Tunnel	300	-	2770	-	600°C 1 hr	Sample bended upon firing
5/5/83	BEA2M	SS1	Zircon Sand	BEA2	Molochite (30-80)	BEA2	Molochite (16-30)	BEA2	Dry slowly	Drying Tunnel	300	2285	-	-	-	Good sample

TABLE 1

EXPERIMENTAL CERAMIC SHELLS

Date	Shell No.	Facecoat		Backup (1&2)		Backup (3&4)		Seal Coat	Dipping Characteristics	Drying Process (2-3days)	De-waxed Temp. (°C)	Cold MOR (Green) lb/in²	Cold MOR (Fired) lb/in²	Hot MOR (Fired) lb/in²	Firing Time & Temp.	Comments
		Slurry	Refr.	Slurry	Refr.	Slurry	Refr.									
5/5/83	BEA3A	SS1	Zircon Sand	BEA3	MgO (30-80)	BEA3	MgO (16-30)	BEA3	Dried quickly	Air	140	-			600°C 1 hr	Good sample
5/5/83	BEA3B	SS1	Zircon Sand	BEA3	Molochite (30-80)	BEA3	Molochite (16-30)	BEA3	Dried OK	Drying Tunnel	140	-	1280		600°C 1 hr	Good sample
5/5/83	BEA3C	BEA3	Zircon Sand	BEA3	Molochite (30-80)	BEA3	Molochite (16-30)	BEA3	OK	Air	140	-	1300		600°C 1 hr	OK
5/5/83	BEA3D	SS1	Zircon Sand	BEA3	Molochite (30-80)	BEA3	Molochite (16-30)	BEA3	OK	Air	140	-	1140		600°C	Good sample
5/5/83	BEA3E	SS1	Zircon Sand	BEA3	Molochite (30-80)	BEA3	Molochite (16-30)	BEA3	OK	Drying Tunnel	140	50	-	-	-	Good green sample
5/5/83	BEA3F	SS1	Zircon Sand	BEA3	Molochite (30-80)	BEA3	Molochite (16-30)	BEA3	OK	Air	140	50	-	-	-	Good green sample
5/5/83	BEA3G	BEA3	Zircon Sand	BEA3	Molochite (30-80)	BEA3	Molochite (16-30)	BEA3	OK	Air	140		-	-	-	Rough surface
5/5/83	BEA3H	BEA3	Zircon Sand	BEA3	Molochite (30-80)	BEA3	Molochite (16-30)	BEA3	OK	Air	140	10	-	-	-	Rough surface
5/5/83	BEA3I	SS1	Zircon Sand	BEA3	MgO (30-80)	BEA3	MgO (16-30)	BEA3	OK	Air	300	740	-	-	-	Good green sample
5/5/83	BEA3J	SS1	Zircon Sand	BEA3	MgO (30-80)	BEA3	MgO (16-30)	BEA3	OK	Air	300	-	-	-	600°C	Poor sample
5/5/83	BEA3K	BEA3	Zircon Sand	BEA3	Molochite (30-80)	BEA3	Molochite (16-30)	BEA3	OK	Air	300	-	1100		600°C	Porous surface
5/5/83	BEA3L	BEA3	Zircon Sand	BEA3	Molochite (30-80)	BEA3	Molochite (16-30)	BEA3	OK	Air	300	1320	-	-	-	Porous surface
5/5/83	BEA3M	SS1	Zircon Sand	BEA3	Molochite (30-80)	BEA3	Molochite (16-30)	BEA3	OK	UT	300	1470	-	-	-	Good sample
5/5/83	BEA3N	SS1	Zircon Sand	BEA3	Molochite (30-80)	BEA3	Molochite (16-30)	BEA3	OK	Air	300	1470	-	-	-	Good sample
5/5/83	BEA3O	SS1	Zircon Sand	BEA3	Molochite (30-80)	BEA3	Molochite (16-30)	BEA3	OK	Air	300	-	1300		600°C 1 hr	Good sample
5/5/83	BEA3P	SS1	Zircon Sand	BEA3	Molochite (30-80)	BEA3	Molochite (16-30)	BEA3	OK	UT	300	-	1300		600°C 1 hr	Good sample

TABLE 4

EXPERIMENTAL CERAMIC SHELLS

Date	Shell No.	Facecoat		Backup (1&2)		Backup (3&4)		Seal Coat	Dipping Characteristics	Drying Process (2-hour)	De-waxed Temp. (°C)	Cold MOR (Green) lb/in²	Cold MOR (Fired) lb/in²	Hot MOR (Fired) lb/in²	Firing Time & Temp.	Comments
		Slurry	Refr.	Slurry	Refr.	Slurry	Refr.									
5/5/83	HEA4A	SSI	Zircon Sand	HEA4	MgO (30-80)	HEA4	MgO (16-30)	HEA4	Dry quickly	Air	140		-	-	-	Good
5/5/83	HEA4B	SSI	Zircon Sand	HEA4	MgO (30-80)	HEA4	MgO (16-30)	HEA4	Dry quickly	Air	140	-			600°C 1 hr	Sample bonked upon firing
5/5/83	HEA4C	SSI	Zircon Sand	HEA4	MgO	HEA4	MgO (16-30)	HEA4	Dry quickly	Air	800	-			600°C 1 hr	Sample bonked upon firing
5/5/83	HEA4D	SSI	Zircon Sand	HEA4	Molochite (30-80)	HEA4	Molochite (16-30)	HEA4	Dry OK (little slowly)	Air	800	-			600°C 1 hr	Sample bonked upon firing
5/5/83	HEA4F	SSI	Zircon Sand	HEA4	MgO (30-80)	HEA4	MgO (16-30)	HEA4	Dry quickly	Air	800		-	-	-	OK
5/5/83	HEA4E	SSI	Zircon Sand	HEA4	Molochite (30-80)	HEA4	Molochite (16-30)	HEA4	Dry slowly	Air	800		-	-	-	OK
5/5/83	SSI	SSI	Zircon Sand	SSI	Molochite (30-80)	SSI	Molochite (16-30)	SSI	OK	Air	140		614	-	600°C 1 hr	Good sample
5/5/83	SSI	SSI	Zircon Sand	SSI	Molochite (30-80)	SSI	Molochite (16-30)	SSI	OK	Air	140		580	-	600°C 1 hr	Good sample
5/5/83	SSI	SSI	Zircon Sand	SSI	Molochite (30-80)	SSI	Molochite (16-30)	SSI	OK	Air	140		580	-	600°C 1 hr	Good sample
5/5/83	SSI	SSI	Zircon Sand	SSI	Molochite (30-80)	SSI	Molochite (16-30)	SSI	OK	Air	140		780	-	600°C 1 hr	Good sample
5/5/83	SSI	SSI	Zircon Sand	SSI	Molochite (30-80)	SSI	Molochite (16-30)	SSI	OK	Air	140		690	-	600°C 1 hr	Good sample
5/5/83	SSI	SSI	Zircon Sand	SSI	Molochite (30-80)	SSI	Molochite (16-30)	SSI	OK	Air	140		680	-	600°C 1 hr	Good sample

A2-4

TABLE 5

EXPERIMENTAL CERAMIC SHELLS

Date	Shell No.	Facecoat		Backup (1&2)		Backup (3-6)		Seal Coat	Dipping Characteristics	Drying Process 2-3days	De-waxed Temp. (°C)	Cold MOR (Green) lb/in^2	Cold MOR (Fired) lb/in^2	Hot MOR (Fired) lb/in^2	Firing Time & Temp.	Comments
		Slurry	Refr.	Slurry	Refr.	Slurry	Refr.									
11/5/83	BEM1A	SS1	Zircon Sand	BEM1	MgO (30-80)	BEM1	MgO (16-30)	BEM1	Dried quickly	Air	140	1064	-	-	-	Facecoat cracked
11/5/83	BEM1B	SS1	Zircon Sand	BEM1	MgO (30-80)	BEM1	MgO (16-30)	BEM1	Dried quickly	Air	140	1122	-	-	-	Facecoat cracked
11/5/83	BEM1C	BEM1	Zircon Sand	BEM1	Molochite (30-80)	BEM1	Molochite (16-30)	BEM1	Dried slowly	Drying Tunnel	140	870	-	-	-	Facecoat cracked
11/5/83	BEM1D	BEM1	Zircon Sand	BEM1	Molochite (30-80)	BEM1	Molochite (16-30)	BEM1	Dried slowly	Drying Tunnel	140	990	-	-	-	Facecoat cracked
11/5/83	BEM2A	SS1	Zircon Sand	BEM2	MgO (30-80)	BEM2	MgO (16-30)	BEM2	Dried quickly	Air	140	1013	-	-	-	Good green sample
11/5/83	BEM2B	SS1	Zircon Sand	BEM2	MgO (30-80)	BEM2	MgO (16-30)	BEM2	Dried quickly	Air	140	1485	-	-	-	Good green sample
11/5/83	BEM2C	SS1	Zircon Sand	BEM2	MgO (30-80)	BEM2	MgO (16-30)	BEM2	Dried quickly	Drying Tunnel	140	1041	-	-	-	Good green sample
11/5/83	BEM2D	SS1	Zircon Sand	BEM2	MgO (30-80)	BEM2	MgO (16-30)	BEM2	Dried quickly	Drying Tunnel	140	837	-	-	-	Good green sample
11/5/83	BEM3A	SS1	Zircon Sand	BEM3	MgO (30-80)	BEM3	MgO (16-30)	BEM3	Dried quickly	Drying Tunnel	140	1047	-	-	-	Good sample
11/5/83	BEM3B	SS1	Zircon Sand	BEM3	MgO (30-80)	BEM3	MgO (16-30)	BEM3	Dried quickly	Drying Tunnel	140	789	-	-	-	Good sample
11/5/83	BEM3C	SS1	Zircon Sand	BEM3	MgO (30-80)	BEM3	MgO (16-30)	BEM3	Dried quickly	Drying Tunnel	140	748	-	-	-	Good sample
11/5/83	BEM3D	BEM3	Zircon Sand	BEM3	Molochite (30-80)	BEM3	Molochite (16-30)	BEM3	Dried quickly	Air	140		-	-	-	Porous surface
11/5/83	BEM3E	SS1	Zircon Sand	BEM3	Molochite (30-80)	BEM3	Molochite (16-30)	BEM3	Dried quickly	Air	140		-	-	-	Good sample

TABLE 6

EXPERIMENTAL CERAMIC SHELLS

Date	Shell No.	Facecoat		Backup (1&2)		Backup (3&4)		Seal Coat	Dipping Characteristics	Drying Process (2-3days)	De-waxed Temp. (°C)	Cold MOR (Green) lb/in^2	Cold MOR (Fired) lb/in^2	Hot MOR (Fired) lb/in^2	Firing Time & Temp.	Comments
		Slurry	Refr.	Slurry	Refr.	Slurry	Refr.									
11/5/83	BEM4A	SS1	Zircon Sand	BEM4	MgO (30-80)	BEM4	MgO (16-30)	BEM4	Dry very quickly	DT	140	-	-	-	600°C 1 hr	Good sample
11/5/83	BEM4B	SS1	Zircon Sand	BEM4	MgO (30-80)	BEM4	MgO (16-30)	BEM4	Dry very quickly	Air	140	-	137		600°C 1 hr	Good sample
11/5/83	BEM4C	SS1	Zircon Sand	BEM4	MgO (30-80)	BEM4	MgO (16-30)	BEM4	Dry very quickly	DT	140	-	124		600°C 1 hr	Good sample
11/5/83	BEM4D	SS1	Zircon Sand	BEM4	MgO (30-80)	BEM4	MgO (16-30)	BEM4	Dry very quickly	DT	140	373.0	-	-	-	Good sample
11/5/83	BEM4E	SS1	Zircon Sand	BEM4	MgO (30-80)	BEM4	MgO (16-30)	BEM4	Dry very quickly	Air	140	397.0	-	-	-	Good sample
11/5/83	BEM4F	SS1	Zircon Sand	BEM4	MgO (30-80)	BEM4	MgO (16-30)	BEM4	Dry very quickly	DT	140	399.0	-	-	-	Good sample
11/5/83	BEM4G	BEM4	Zircon Sand	BEM4	Molochite (30-80)	BEM4	Molochite (16-30)	BEM4	Dry very slowly	DT	140	-	-	-	-	Rough porous surfaces
11/5/83	BEM4H	BEM4	Zircon Sand	BEM4	Molochite (30-80)	BEM4	Molochite (16-30)	BEM4	Dry very slowly	DT	140	-	-	-	-	Rough porous surfaces
11/5/83	BEM4I	BEM4	Zircon Sand	BEM4	Molochite (30-80)	BEM4	Molochite (16-30)	BEM4	Dry very slowly	DT	140	-	1097.0		600°C 1 hr	Rough porous surfaces
11/5/83	BEM4J	BEM4	Zircon Sand	BEM4	Molochite (30-80)	BEM4	Molochite (16-30)	BEM4	Dry very slowly	DT	140	-	-	-	600°C	Rough porous surfaces
11/5/83	BEM4K	SS1	Zircon Sand	BEM4	Molochite (30-80)	BEM4	Molochite (16-30)	BEM4	Dry slowly	Air	140	-	-	-	600°C 1 hr	Good sample
11/5/83	BEM4L	SS1	Zircon Sand	BEM4	Molochite (30-80)	BEM4	Molochite (16-30)	BEM4	Dry slowly	Air	140	-	1295.0	-	600°C 1 hr	Good sample
11/5/83	BEM4M	SS1	Zircon Sand	BEM4	Molochite (30-80)	BEM4	Molochite (16-30)	BEM4	Dry slowly	Air	140	-	1409.0	-	600°C 1 hr	Good sample
11/5/83	BEM4N	SS1	Zircon Sand	BEM4	Molochite (30-80)	BEM4	Molochite (16-30)	BEM4	Dry slowly	Air	140	-	-	-	600°C 1 hr	Good sample

TABLE 7

EXPERIMENTAL CERAMIC SHELLS

Date	Shell No.	Facecoat		Backup (1&2)		Backup (3-6)		Seal Coat	Dipping Characteristic	Drying Process (2-3days)	De-waxed Temp. (°C)	Cold MOR (Green) lb/in²	Cold MOR (Fired) lb/in²	Hot MOR (Fired) lb/in²	Firing Time & Temp.	Comments
		Slurry	Refr.	Slurry	Refr.	Slurry	Refr.									
11/5/83	BEM4O	SS1	Zircon Sand	BEM4	Molochite (30-80)	BEM4	Molochite (16-30)	BEM4	Dry slowly	Air	140	Did not break (plasticity)	-	-	-	Good sample
11/5/83	BEM4P	SS1	Zircon Sand	BEM4	Molochite (30-80)	BEM4	Molochite (16-30)	BEM4	Dry slowly	Air	140	Did not break (plastic	- behaviour)	-	-	Good sample
11/5/83	BEM4Q	SS1	Zircon Sand	BEM4	Molochite (30-80)	BEM4	Molochite (16-30)	BEM4	Dry slowly	DT	140	-	1305		600°C 1 hr	Good sample
11/5/83	BEM4R	SS1	Zircon Sand	BEM4	Molochite (30-80)	BEM4	Molochite (16-30) .	BEM4	Dry slowly	DT	140	-	1335		600°C 1 hr	Good sample
11/5/83	BEM4S	SS1	Zircon Sand	BEM4	Molochite (30-80)	BEM4	Molochite (16-30)	BEM4	Dry slowly	DT	140	1.6	-	-	-	Good sample
11/5/83	BEM4T	SS1	Zircon Sand	BEM4	Molochite (30-80)	BEM4	Molochite (16-30)	BEM4	Dry slowly	DT	140		-	-	-	Good sample
11/5/83	BEM4U	SS1	Zircon Sand	BEM4	Molochite (30-80)	BEM4	Molochite (16-30)	BEM4	Dry slowly	DT	140		-	-	-	Good sample
11/5/83	BEM3F	SS1	Zircon Sand	BEM3	MgO (30-80)	BEM3	MgO (16-30)	BEM3	Dry slowly	DT	140	-		260	600°C 1 hr	Good sample
11/5/83	BEM3G	SS1	Zircon Sand	BEM3	MgO (30-80)	BEM3	MgO (16-30)	BEM3	Dry slowly	DT	140	-		165	600°C 1 hr	Good sample
11/5/83	BEM3H	SS1	Zircon Sand	BEM3	MgO (30-80)	BEM3	MgO (16-30)	BEM3	Dry slowly	DT	140	-		225	600°C 1 hr	Good sample
11/5/83	BEM3I	SS1	Zircon Sand	BEM3	Molochite (30-80)	BEM3	Molochite (16-30)	BEM3	Dry slowly	DT	140	-		1173	600°C 1 hr	Good sample
11/5/83	BEM3J	SS1	Zircon Sand	BEM3	Molochite (30-80)	BEM3	Molochite (16-30)	BEM3	Dry slowly	Air	140	-		940	600°C 1 hr	Good sample

TABLE 8

MOR RESULTS OF FLYASH SAMPLES (FIRED)

SAMPLE FLYASH	MOR lb/in^2	AVERAGE lb/in^2
AFAC 1	154.8	
2	113.3	153
3	192.2	
AFAD 1	792.2	
2	779	
3	608	745
4	728	
5	819	

TABLE 9

MOR RESULTS OF SILICA FUME SAMPLES

SAMPLE		MOR lb/in^2	AVERAGE lb/in^2
AFSA	1	-	-
	2	703.7	
(FIRED)	3	750	685
	4	559	
	5	614	
	6	795	
AFSA	7	99.0	
	8	118	
(GREEN)	9	115	100
	10	100	
	11	68	
AFSB	1	547	
	2	390	
(FIRED)	3	383	415
	4	380	
	5	301	
	6	487	
AFSB	7	87	
	8	81	
(GREEN)	9	111	97
	10	94	
	11	100	
	12	107	

TABLE 9 (continued)

SAMPLE		MOR lb/in^2	AVERAGE lb/in^2
AFSC	1	466	
	2	525	
(FIRED)	3	458	482
	4	514	
	5	435	
	6	495	
AFSC	7	120.7	
	8	145	
(GREEN)	9	170	146
	10	149	
AFSD	1	337	
	2	328	
(FIRED)	3	357	315
	4	276	
	5	313	
	6	276	

TABLE 10

MOR RESULTS OF ZIRCON/FUSED SILICA MAP SAMPLES

SAMPLE		MORE lb/in^2	AVERAGE MOR lb/in^2
DA-15	1	434.4	
	2	597	532
(FIRED)	3	677	
	4	465	
	5	487	
DA-15	1	262	
	2	89	217
(GREEN)	3	239	
	4	276	
DA-25	1	463	
	2	845	769
(FIRED)	3	840	
	4	930	
DA-45	1	73.0	
	2	63	74
(GREEN)	3	73	
	4	86	
DA-45	1	689	
	2	836	937
(FIRED)	3	1081	
	4	1199	
	5	1032	
	6	787	
DA-65	1	1486	
(FIRED)	2	1386	1462
	3	1514	

TABLE 11

MOR RESULTS OF PROMISING SAMPLES

SAMPLE		MOR lb/in^2	AVERAGE MOR lb/in^2
DA-45	1	1320	
Dried in air	2	1309	1307
(Fired at	3	1275	
600°C)	4	1322	
DA-45	1	946	
Dried in air	2	1014	1098
(Fired at	3	1104	
800°C)	4	1193	
	5	1129	
	6	1203	
DA-45	1	73.0	
Green	2	63	74
Dried in air	3	73	
	4	06	
DA-45	1	779	
Dried with	2	576	743
NH_3	3	927	
GREEN	4	722	
	5	641	
	6	810	
DA-45	1	927	
(Fired at	2	536	
600°C)	3	497	637
Dried in NH_3	4	846	
	5	498	
	6	521	
DA-45	1	967	
Dried in NH_3	2	774	879
Fired at	3	1062	
800°C	4	774	
	5	784	
	6	914	

ORE

TABLE 12

HOT MOR RESULTS (600°C)

SAMPLE		MOR lb/in^2	AVERAGE MOR lb/in^2
DA-15	1	557.2	457
	2	357.5	
DA-25	1	331.6	912
	2	1492.6	
DA-45	1	1165.2	1264
	2	1363.3	
DA-65	1	1224	1355
	2	1486	
AFSA	1	642	593
	2	544	
AFSB	1	270	300
	2	302	
	3	327	
AFSC	1	398	407
	2	491	
	3	332	
AFSD	1	274	350
	2	426	

TABLE 13

HOT MOPE RESULTS (AT 600°C)

SAMPLE		MOR lb/in^2	AVERAGE MOR lb/in^2
FUMED SILICA AFSA	1	630	640
	2	649	
AFSB	1	313	258
	2	195	
	3	266	
AFSC	1	344	340
	2	377	
	3	248	
AFSD	1	251	342
	2	433	
DPC MAP SAMPLE			
DA-25	1	130.6	193
	2	255.6	
DA-15	1	416	327
	2	237	
DA-65	1	Warped, did not	
	2	break	
DA-45	1	Warped, did not	
	2	break	

POOR

QUALITY

ORIGINAL